

UTILIZATION OF BLASTFURNACE SLAG IN MAKING CEMENTS

By
VIKRAM PRATAP MEHROTRA

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UTILIZATION OF BLASTFURNACE SLAG IN MAKING CEMENTS

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VIKRAM PRATAP MEHROTRA

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CERTIFICATE

This is to certify that this work entitled,
"UTILIZATION OF BLASTFURNACE SLAG IN MAKING CEMENTS" by
V.P. Mehrotra has been carried out under our supervision
and has not been submitted elsewhere for a degree.

A.S.R. Sai

Dr. A.S.R. Sai
Assistant Professor
Dept. of Civil Engineering
Indian Institute of Technology
Kanpur

P.C. Kapur

Dr. P.C. Kapur
Professor
Dept. of Metallurgical Engg.,
Indian Institute of Technology
Kanpur

Kanpur
July, 1976

POST GRADUATE OFFICE
This thesis has been approved
for the award of the degree of
Master of Technology (M.Tech.)
in accordance with the
regulations of the Indian
Institute of Technology Kanpur
Dated. 29.7.76 24

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TABLE OF CONTENTS

CHAPTER	Page
LIST OF TABLES	iv
NOTATION	v
1. INTRODUCTION	1
1.1 Objective of the Present Study	6
2. LITERATURE SURVEY	9
2.1 Blastfurnace Slag	9
2.2 Granulated Slag: Constitution and Properties	11
2.3 Slag Cements	38
2.4 Effect of Temperature on Cement Properties	59
2.5 Summary of Literature Survey	62
3. EXPERIMENTAL PROCEDURE RESULTS AND DISCUSSION	65
3.1 Experimental Procedure	65
3.2 Results and Discussion	72
4. CONCLUSIONS AND SCOPE FOR FUTURE WORK	108
REFERENCES	113
APPENDICES	117

LIST OF TABLES

	Page
2.1 Chemical compositions of blastfurnace slag and Portland cement	10
3.1 Chemical composition of TISCO blastfurnace slag	65
3.2 Initial and final setting times of Portland blastfurnace slag cements	75
3.3 Compressive strength values of 1:2:4 concrete cubes of supersulfated composition V	81
3.4 Effect of additives on initial setting time of composition V	85
3.5 Initial setting times of hard burnt gypsum and plaster of Paris mixture activated composition V	91

NOTATION

The following abbreviated formulae are used in the text:

C = CaO; A = Al₂O₃; S = SiO₂; F = Fe₂O₃; M = MgO;
H = H₂O.

CS = CaO.SiO₂
C₂S = 2CaO.SiO₂
C₃S = 3CaO.SiO₂
C₂AS = 2CaO.Al₂O₃.SiO₂
CAS₂ = CaO.Al₂O₃.2SiO₂
C₂MS₂ = 2CaO.MgO.2SiO₂
CMS = CaO.MgO.SiO₂
C₅AS = 5CaO.Al₂O₃.SiO₂
CMS₂ = CaO.MgO.2SiO₂
C₂ASH₈ = 2CaO.Al₂O₃.SiO₂.8H₂O
C₂AH₈ = 2CaO.Al₂O₃.8H₂O
C₃ASH₄ = 3CaO.Al₂O₃.4H₂O

ABSTRACT

Blastfurnace slag which is a by-product of steel industry has been tried for making Portland blastfurnace slag cement and supersulfated cement. Results of the strength tests on Portland blastfurnace slag cement show that it is possible to make slag additions at least up to 20% without sacrificing much of the strength. Similarly in the case of supersulfated cement it has been shown that this cement after a few weeks hydration gives better strength than that obtained with Portland cement and hence it can be a suitable alternative for Portland cement. Further, it is shown in this study that plaster of Paris is a better activator than the conventional hard burnt gypsum which has so far been used in the production of supersulfated cement in other countries. The short setting time of the supersulfated cements using plaster of Paris as an activator can be increased by small additions of borax.

The X-ray analysis of supersulfated cements show that calcium silicate, calcium aluminate hydrates, tobermorite and ettringite are the main hydration products. DTA analysis also shows the presence of tobermorite and ettringite phases.

High temperature studies show supersulfated cement to be better than Portland cement as far as stability towards lime hydration is concerned but severe reduction in strengths with temperature makes it an unsuitable refractory cement.

CHAPTER 1

INTRODUCTION

It is now fifty years since the production of Portland cement began in India. During this period there has been a progressive increase in the output of the cement and this has been particularly rapid since the five years plans were initiated. Today, the annual production of cement stands at about 15 million tonnes. The demand has, however, grown at a much faster rate and despite the efforts of the cement industry the gap between the supply and the demand still remains unbridged.

The principal raw materials used in the manufacture of cement are:

1. Argillaceous, or silicates, of alumina in the form of clays and shales.
2. Calcareous, or calcium carbonate, in the form of limestone, chalk and marl which is a mixture of clay and calcium carbonate.

The ingredients are mixed very roughly in the proportion of two parts of calcareous material to one part of argillaceous material. The mixture is then ground wet or dry in a ball mill, and subsequently clinkered in

either a rotary or a shaft kiln. The maximum temperature attained in the kiln lies in the range 1400°C and 1500°C , pulverised coal, gas or oil being used as the fuel. The clinker from the kiln is first cooled and then ground in a ball mill, along with an addition of gypsum, to the requisite fineness according to the class of product.

The deceptive simplicity of the manufacture of cement by the process explained above is exposed when one ventures to establish a plant. Apart from the technological aspects, there are several hurdles, which a prospective manufacturer faces, making the whole integrated industry a highly capital intensive.

To fulfil the immediate demands of the nation's constructional needs, there are two alternatives, either to set-up new cement plants or use alternative building materials. As stated above setting up a cement plant requires massive doses of investment and time with limited employment potentials. So the only alternative open is to develop and use other alternative materials for making cement.

Blastfurnace slag which is a by-product obtained in the manufacture of pig iron in the blastfurnace is a major waste material in the steel industry. This industrial waste material when treated specially can be profitably

used in making cement and other building materials. Making cement from blastfurnace^{slag} helps in two ways. Firstly the cement made from slag has certain beneficial properties and secondly the utilization of industrial waste product is in itself economically desirable.

For each tonne of pig iron produced in the blastfurnace a by-product of $\frac{3}{4}$ to 1 tonne of slag is left behind, and its disposal poses a major problem. This proportion of slag to iron produced by the blastfurnace varies with the richness in iron content of the ore and size and efficiency of the furnace. A very major portion of slag so far has been dumped in unseemly heaps near the plants. Of the 6 million tonnes of slag per annum now available in India, only half a million tonne is used at present. This can easily be increased to 3-4 million tonnes. Utilization of the slag in cement industry will not only make an efficient but a maximum possible use of a by-product that has a commercial value and in reality a national asset that we cannot afford to waste.

Conversion of blastfurnace slag, which issues from the blastfurnace as a molten stream at a temperature of 1400-1500°C, into products suitable for various uses depends on its type and subsequent processing. Blastfurnace slags can be divided into two types¹. (i) Those

arising from acidic iron ores and (11) those from basic iron ores. But due to the method of furnace operation, these are in fact similar. In countries where magnetite and haematite are the principal sources of iron, acid (siliceous) slags result, on the other hand, with calcareous ores much of the slag is basic (limy). Clearly with the variations in analysis as mentioned above there will be variations in uses to which slags can be put. Slags depending upon their processing and compositions have found a considerable use in the following fields.

1. Slag aggregates:

Undoubtedly the largest tonnage of slag that finds industrial applications is as slag aggregate. This is produced when the slag is allowed to cool slowly thereby solidifying in a gray, crystalline, stony material, known as air-cooled, lump or dense slag. This is used for road making, ballast for railway lines and other applications requiring inert classified material. More rapid chilling with a limited amount of water, applied in such a way as to trap steam in the mass, produces a porous, honeycombed material which resembles pumice. This lightweight material, called foamed slag, is used after crushing and grinding as a lightweight aggregate.

2. Granulated cement:

When the slag aggregate is ground to a very fine powder, it may be used as filler in the preparation of slag cements.

3. Glass:

If the chemical analysis is right and there is no incidence of dissolved metallic phases in the slag, it may be possible to use the resultant granulated product as a raw material in the manufacture of glass. Glass bottles have been made from this material.

4. Slag wool:

There has been a considerable interest in recent years regarding the manufacture of slag wool. This product is an excellent inert thermal insulator. The general method of producing this type of product is to charge the powdered raw material and coke in a cupola, and melt the charge at 1400°C . The molten slag stream is allowed to fall into a convergent jet of high pressure steam. The force of the jet breaks the molten slag into small globules which as they are blown forward become fine fibres.

Slag which is to be used in the manufacture of various slag cements (to be discussed later) is chilled

very rapidly either by pouring into a large excess of water or by subjecting the slag stream to jets of water or of air and water. The purpose is to cool the slag quickly so that crystallization is prevented and it solidifies as a glass. At the same time the quenching breaks-up the material into small particles varying from glassy beads to a light weight froth. The product is called granulated slag and is primarily used as a cement of one type or another. Minor quantities are sold for glass making, as abrasive and as sand filler for concrete.

The ease with which this granulation can be done depends upon the chemical composition of the slag and on the temperature at which it comes out of the furnace. Siliceous slags cool to glasses most easily while prevention of crystallization is more difficult for slags with high lime content.

1.1 Objective of the Present Study

Large amounts of slag can be consumed in making cement, therefore, the main objective of this study was to see the feasibility of using granulated blastfurnace slag as a partial replacement of Portland cement in concrete or in making supersulfated cement. This will not

only be an efficient way of disposing of the waste but also helpful in fulfilling the country's demand for constructional work.

The study on supersulfated cement included the following tests:

- (1) Compressive strength determination of 1:3 mortars and 1:2:4 concrete mixtures as a function of curing age.
- (2) Determination of setting times.
- (3) X-ray and DTA examination of hydrated samples.

Supersulfated cement has no or very little free lime after hydration, which being there in Portland cement makes it unsuitable for refractory cement. This led to the study of high temperature properties of the former cement. Here tests were done to determine the effect of firing temperature on the compressive strength. Since for a refractory material expansion/shrinkage during first heating/cooling cycles are very important, therefore these values were also measured.

In addition to supersulfated cements Portland blastfurnace slag cement mixtures were also prepared and tested for strength. Only lesser additions up to 20 per cent were tried to see whether it is always possible to

blend the Portland cement with a little percentage of slag without much affecting the properties of Portland cement.

Apart from making cement for building works, attempts were made to explore the possibility of using supersulfated cement as a binder material for making cold bonded iron ore pellets for blastfurnace charge. Because of some experimental difficulties and non-availability of facilities the problem could not be completed.

CHAPTER 2

LITERATURE SURVEY

2.1 Blastfurnace Slag

Blastfurnace slag is the molten flux in the blastfurnace which contains the unreduced oxides in the production of pig iron. It is produced from the silicates, argillaceous and calcareous constituents of the iron ore together with the ashes from coke fuel and limestone added as a flux. That is, when the iron ores, which are mainly oxides of iron, are mixed with coke and limestone and heated to a temperature of 1560°C , the iron oxide combines with carbon from coke to give CO and CO_2 . The ore is reduced in this process to metallic iron which melts and collects as a liquid in the hearth of the furnace.

The iron ore contains impurities which are usually clayey in nature consisting of mixture of silica and alumina whose fusion temperature is much higher than the melting point of iron. As it is difficult to separate these impurities from the molten iron in solid state, a quantity of lime is added to the blastfurnace charge of iron ore and coke so as to facilitate the formation of an easily fusible mixture of lime, silica and alumina.

As a consequence of this a surface layer of molten slag floats on top of heavier molten iron which is discharged from the blastfurnace in the liquid state. The main constituents of slag are therefore nearly the same as those of Portland cement i.e. lime, silica and alumina but in different proportions. Chemical compositions of typical Indian slag is given in Table 2.1. For comparison sake chemical composition of ordinary Portland cement is also given.

Table 2.1

Chemical compositions of blastfurnace slag and Portland cement

Oxides	Blastfurnace slag	Portland cement
	Wt%	Wt%
Lime (CaO)	30-38	60-67
Silica (SiO ₂)	29-37	17-25
Alumina (Al ₂ O ₃)	18-33	3-8
Magnesia (MgO)	3-7	0.1-4
Iron oxide (Fe ₂ O ₃)	1	0.5-6
Sulfur trioxide (SO ₃)	1	1-3
Soda and/or potash (Na ₂ O + K ₂ O)	—	0.5-1.3

Composition of slag² can vary over a wide range depending on the nature of the ore, the compositions of limestone and coke, and the kind of iron being made. It can also change over the years with alterations in the sources and kinds of ore being smelted. These variations affect the relative contents of the four major constituents, lime, silica, alumina and magnesia and also the amounts of minor components, sulfur in the form of sulfides and ferrous and manganese oxides.

If the chemical compositions of slag and Portland cement are compared, one can immediately note that slag contains less lime than Portland cement. Addition of limestone to the charge to such an extent as to give a slag with a composition of Portland cement would kill the very purpose of the addition of limestone to the charge, since then the resulting mixture will not have a low melting point.

2.2 Granulated Slag: Constitution and Properties

2.2.1 Physical State and Hydraulicity:

It is a characteristic feature of silicate melts that on rapid cooling from the liquid state they tend to form glass. The passage from the liquid to a crystalline

solid condition is accompanied by a rearrangement of the ions which take up a definite orientation in the crystals, and the viscosity of the molten silicates near the freezing point is so large that this rearrangement only takes place slowly. If the cooling is rapid the ionic groups largely retain their irregular arrangement; and with the viscosity increasing rapidly as the temperature falls, the slag passes from the liquid state to one in which the rigidity approaches that of a solid, but without the development of a crystalline structure. When powdered granulated slag is examined on a microscope slide by transmitted light, the glass is seen to consist of clear isotropic transparent grains. Less perfectly granulated slags may show brown or black zones where incipient crystallization has begun.

It is generally believed that increasing amounts of crystalline components reduce the cementing properties though some of them may make some contribution to the strength. Usual compositions of different commercial slags lie within the primary fields of C_2AS and CAS_2 in the phase equilibrium diagram (Fig. 1) of the system $CaO - Al_2O_3 - SiO_2$ and hence the primary products of crystallization of such slags are C_2AS and CAS_2 . These two compounds have no hydraulic property and as a result

the activity of commercial slags fall if crystallized. To avoid crystallization molten slag is quenched to glassy granulated state.

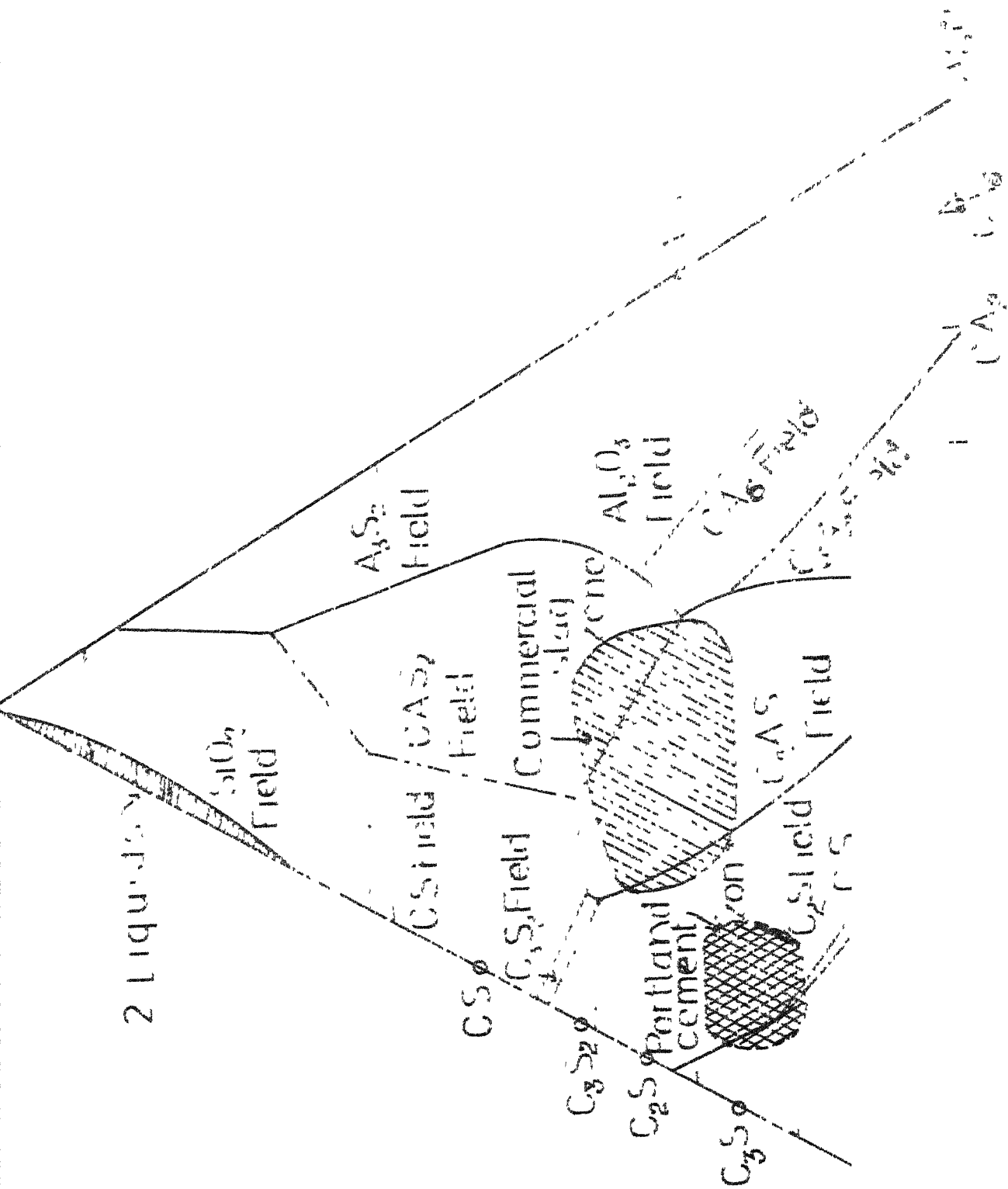
This granulated slag alone has no or very little cementing characteristics, but if, some suitable activator is present it may show marked cementitious properties. The activator may be lime, Portland cement, alkalis such as caustic soda, or sodium carbonate or the sulfate of the alkalis, lime or magnesia. It is, of course, this property which has led to the use of this material in various forms of cement.

The function of the activators is to initiate the decomposition reaction leading to the formation of hydrated cementing compounds. According to Locher³ these chemical activators provide a chemical composition in the solution such that the ions dissolved from the slag can rapidly form strength producing hydrate phases. Activators also open up the silicate structure of the glass so as to accelerate the rate of hydration. Thus a lime activator prevents the formation of an impermeable alumino-silicate film and progressively combines with slag. In the case of sulfate activators the initial attack will be on the alumina to form calcium sulfoaluminate and this must be presumed to open up the silicate structure.

In general, the hydraulicity of the granulated blastfurnace slag is closely related to the chemical composition of the slag and usually, the higher the basicity of the slag the greater is its hydraulicity. Different formulae have been suggested from time to time assuming that CaO or the basic oxides have a positive effect, whereas SiO_2 or the acid constituents have negative influence on the hydraulicity. Aluminium oxide has been known to be a very important constituent and is considered partially basic and partially acidic.

The cause of this hydraulic activity and its relation to the chemical composition and physical state of a slag has been studied extensively without reaching finality as yet. The glass content is a prime factor in determining the hydraulicity of the product. For a series of haematite slags quenched to give varying glass contents, Schwiete and Dolbar⁴ obtained a roughly linear relation between strength and glass content. Any imperfections in granulation technique leads to partial crystallization of the slag thus affecting its hydraulicity⁵. Portland cement on the other hand is essentially a crystallized material and its hydraulicity is not dependent on its glass content. This is due to the fact that composition of Portland cement is different from that

of the slags as will be evident from Fig. 1. Figure 1 shows that the primary products of crystallization of commercial slags as mentioned before are C_2AS and CAS_2 which have no hydraulic properties whereas in Portland cement the crystalline products are the various hydraulic compounds such as C_2S , C_3S etc. Glassy slags are active most probably because of their higher free energy than crystallized slags. However Solacolu⁶ has expressed doubts about the authenticity of this fact and mentioned that the small difference in the free energy between the glassy and crystallized slags is not sufficient to explain the hydraulicity of the glassy slags. Solacolu has observed highly crystalline slags with good hydraulicity. Mukherjee and Chatterjee⁵ have observed that in slags, where crystallization products are found to be non-hydraulic, the hydraulicity is less. In some cases non-hydraulic C_2S polymorphic form is formed on crystallization, even then, the hydraulic activity is improved. This may be because of the crystallization of only C_2S and consequent increase in Al_2O_3 content, in the remaining glassy portion, which as discussed later might improve the hydraulicity. Some slags whose glassy form is almost non-hydraulic may become hydraulic on crystallization if the crystallized products are hydraulic.



2.2.2 Mineralogical Composition and Hydraulicity:

Attempts have also been made relying on the phase relationships in equilibrium crystallization, to convert the analyses of the basic blastfurnace slag glasses, after grouping them in a quaternary system $(Ca, Na_2)O - MgO - (Fe, Mn)O - Al_2O_3 - SiO_2$ into compounds. The following were selected:

Akermanite	C_2MS_2	Wollastonite	CS
Gehlenite	C_2AS	Monticellite	CMS
Dicalcium silicate		$5CaO, 3Al_2O_3$	C_5A_3
	C_2S		

An attempt, based on comparison of hydraulic behaviour of slag glasses in which the one or the other constituent was numerically predominant, was made to determine the hydraulic efficiency of these assumed compounds.

There is no direct relationship between the content of C_2S , the melilite* solid solution and C_2MS_2 and the hydraulic activity of the slags but the more markedly active slags are those which contain these

* Melilite is the name given to an isomorphous series of solid solutions of which the two principal end members are gehlenite and akermanite.

components as potential phases. Slags which on complete crystallization give phases of low lime content such as CS and C_2S_2 have poor hydraulic properties⁷.

The selected compounds are not all the crystal types occurring at equilibrium in the system C-M-A-S. In particular, Al_2O_3 still present after the calculation of gehlenite was calculated as calcium aluminate, in order to take into account the peculiar hydraulic behaviour of high alumina bearing basic slag glasses, while spinel should be formed at equilibrium with basic blastfurnace slags of the usual MgO content. On the basis of tests, it has been shown that the hydraulic behaviour of the glasses concerned cannot be properly evaluated by converting the analysis into minerals present at equilibrium.

2.2.3 Investigations with Synthetic Melts:

Numerous investigations have been made on pure synthetic glasses in an endeavour to determine the optimum composition. The results of tests on ground glasses of pure compound composition are not entirely concordant.

Keil⁸ has reported some results on pure glasses with the chemical composition of gehlenite and of akermanite. It was revealed that gehlenite glass and the

two similar mixes possess no hardenability of their own and react either very little or not at all after sulfate activation or with activation as slag-Portland cement, but attain very considerable strengths with Ca(OH)_2 as activator. Akermanite glass is self hardening in a remarkable way (122 Kg/Sq.cm. compressive strength at 28 days stored in water), a conclusion supported by Butt⁹, but Budnikov¹⁰ found no strength development. It may well be that temperature of preparation of glass has some influence. Akermanite glass develops higher strength as slag-Portland cement than gehlenite glass, but with lime hydrate it has considerably lower strength than gehlenite glass and the gehlenite-like glasses. Thus, it may be stated here that no support has been found for the belief that the hydraulic properties of blastfurnace slags are the result of certain chemically defined groupings such as gehlenite and akermanite or are determined by the minerals in equilibrium crystallization.

Furser and Stutterheim¹¹ have investigated the gehlenite-Spinel system and found that the greater part of the system lies within the spinel primary phase field and that the eutectic at 1527°C has a composition of about 85.5 per cent gehlenite and 14.5 per cent spinel (CaO 34.15 per cent, MgO 4.70 per cent, Al_2O_3 42.85 per cent,

SiO_2 18.30 per cent). As regards the hydraulic properties of these glasses, it has already been said, beyond a certain content, MgO must not be regarded as hydraulically effective component, apparently because it crystallizes out as a spinel.

2.2.4 Reactivity of Granulated Slag:

The reactivity of granulated slag must be related to the structure of the glass and the ease with which hydration can occur. A good number of workers⁴ have used Zachariasen's¹² network theory of glass formation to explain the constitution of slag glasses. This theory postulates the formation of networks of oxygen tetrahedra such that, although there is no periodicity of structure which would yield a sharp X-ray pattern, the statistical arrangement is similar to the ordered arrangement of crystalline state. In slags the network forming cations are silicon and aluminium which link together by sharing the oxygen atoms of the tetrahedra. Calcium and magnesium ions occupy the relatively large voids in the network structure and are known as network modifiers. Aluminium ions can act as a network former or modifier, but they can only replace Si ions to a limited extent and in so

doing they increase the interionic distance between the cation and the oxygen ions. This increases the specific volume of the glass and produces a more open network that can accommodate more of the larger Ca ions in the voids in the structure. The hydraulic behaviour of the slag may be expected to depend on the extent to which aluminium ions are present as network formers, giving an aluminium silicate network, and the extent to which they are present as network modifiers occupying voids in the structure. The nature of the hydration products will be determined by the lime concentration in the solution and this will depend on the activator and on the rate of supply of Ca ions from the voids in the glass network.

Another theory¹³ of glass structure known as the crystallite theory, postulates a 'micro heterogeneity' in glasses. A glass is considered to contain short range domains in which there is a certain degree of order, or, as they have been termed, 'embryos of crystallization'. The regions contain most of the cations and are linked together by amorphous regions formed by the remaining anions. DeLangavent¹⁴ has suggested that in the liquid slag there is a tendency for polymerised Si_xO_y groups to exist as a framework of chains or hands, leaving a higher ratio of base to acidions amongst the other constituents

of the melt. Very hot slags cannot sometimes be chilled to a glass and this is attributed to fracture of the silica network with the loss of its inhibiting effect on crystallization. The theory of liquid slag structure and its possible relations to the properties of the granulated slag are reviewed by Shröder⁴.

The difference between the network and the crystallite theories of the glass structure may well be abridged as more information becomes available but it is clear that the mineral compounds do not exist as such when a slag is in the vitreous state and that there is some form of two-region structure.

Having discussed the effect of physical state and the mineral constitution at equilibrium it is worthwhile to see the effect of various oxides and other constituents of the slag on its hydraulicity.

2.2.5 Chemical Composition and Hydraulicity:

The influence of chemical composition² on the hydraulicity of the granulate is complex since it affects the slag temperature and granulation condition, as well as, the intrinsic properties of the glass.

Experiments on the hydraulic properties confirm unanimously that the hydraulic value of a slag rises with an increasing content of CaO upto a point when increasing CaO content makes granulation to glass difficult. Hydraulic value of slag decreases with increasing amount of SiO_2 and MnO , and perhaps also TiO_2 and FeO . High calcium sulfide content is favourable. Slags high in calcium sulfide behave somewhat characteristically. These are self-stimulating by the hydrolysis of sulfide, with formation of lime hydrate which then acts as a secondary stimulator. Such slags develop direct, rather than latent hydraulicity. But the CaS of common blastfurnace slags evolves hydrogen sulfide in slag cements in contact with acidic solutions and make them unsuitable for construction of food silos in which organic acids (chiefly acetic and lactic acid, sugars and the like) occur. Langavant¹⁵ demonstrated how this troublesome evolution of hydrogen sulfide can be overcome when the surface of hardened slag cement mortars or concrete is treated with 10 per cent solution of sodium bisulfite which immediately reacts to form sulfate and finely dispersed sulfur.

At constant basicity the strength increases with the Al_2O_3 content and a deficiency in CaO can be compensated by larger amount of alumina. It has been shown by

Kolhatkar et al¹⁶ that strength is markedly influenced by alumina as well as the granulation temperature of the slag. It is found that 1 per cent increase in alumina content increases the granulation liquidus by about 10 per cent. At a finite alumina content, rise in granulation temperature is accompanied by an increasing trend in strength. The observed decrease in tensile strength by these workers with increasing alumina content above a certain limit is inferred to be due to certain changes in glassy structure.

At lower alumina content, the glass would be of $\text{CaO-Al}_2\text{O}_3$ structure which is associated with fairly rapid hydration. The reported findings of Keil that slags containing 8-15 per cent alumina hydrate faster than lower alumina slag should be due to the increasing predominance of the above glassy structure as the alumina content increases. Further increase in alumina introduces a change in the structures of $n \text{ CaO}-2\text{Al}_2\text{O}_3$ which hydrates much more slowly than the faster monomolecular combination. The findings that the hydration is retarded with increasing alumina in the range of 25 to 32 per cent seems to be due to the increasing proportion of the above polymolecular configuration in the glassy structure.

The foregoing views on the effect of CaO and Al_2O_3 on the hydraulicity of slags have been supported by other workers also. Gupta and Lahiri¹⁷, with lime slag mixes, have shown that compressive strength which is a measure of its hydraulicity increased with increase in Al_2O_3 content of slag. Even slags rich in CaO showed poor strengths when Al_2O_3 content was very low, however at constant alumina, strength increased with increasing CaO content. Tanaka¹⁸ has concluded that at early ages the compressive strength becomes higher with the increase in CaO content of the slags, and that the rate of strength increase becomes faster with the decrease in CaO content as long as Al_2O_3 is about 16 to 22 per cent. Apart from directly influencing the hydraulic value of the slag, alumina content has some indirect effect also. The grindability of slag decreases with increase in the alumina content and this may influence the economics of slag cement production as these cements are ground finer than ordinary Portland cement.

Regarding the effect of SiO_2 , it was mentioned before that it decreases the hydraulic value of the slag, but it has been observed¹⁸ in syntactic slags that when SiO_2 content of slag was decreased to less than 25 per cent, the hydraulicity tended to recover gradually and

by further decrease in SiO_2 so as to enter the region of aluminous cements, the slag began to show the self hardening property, and even caused flash set when activated by Portland cement.

An important practical problem in slag cements is the permissible maximum amount of magnesia as a constituent of blastfurnace slags. Budnikov and Kosyreva²⁰ studied mixes of slags with upto 10 per cent magnesia either in the slag itself or introduced as dolomite. For the first type, the mechanical strength of the cement products increased with increasing original magnesia content of the slag with an optimum at 7 per cent, whereas the addition of dolomite was slightly detrimental. Magnesia containing slags are highly corrosive for refractories. In the opinion of Budnikov and Kosyreva, it is possible that during slag granulation a complex compound containing magnesia is decomposed which makes it highly reactive. Another particularly interesting aspect of the same problem was given by Cirilli and Brisi²¹ for slags containing upto 33 per cent MgO which was formed by devitrification of forsterite and moticellite, but no free periclase. The hydraulic properties of these slags were not only normal but quite good, no sensible expansions of autoclave test samples could be observed. In many iron mills it is impossible to

exclude dolomitic limestones from mixing in blastfurnace charges and it is then a serious problems to sustain the strict specifications keeping magnesia contents in hydraulic binders, of Portland blastfurnace slag type, at an upper limit of 3 to 5 per cent²². Evidently highly magnesia bearing blastfurnace slags are often in no way detrimental to volume stability of the cement products.

Of paramount importance is the necessity to impede crystallization of free periclase which is the source of serious volume instability of hydraulic binders. Its presence is immediately indicated by the autoclave soundness test. By slow crystallization periclase really is observed in certain high magnesia slags. But, as long as melilites and monticellite are the only magnesia containing minerals in the slags, no volume instabilities occur. Spinel would equally be fully inert and secondary formation of brucite by reaction in the cement setting process cannot affect the volume stability. Previous studies of Langavant²³ confirm that in normal blastfurnace slags crystallization of periclase is excluded which is in agreement with observations of other workers. In his opinion, magnesia rich slag cements are even favourable for improved corrosion resistance.

Keil et al observed that slags rich in magnesia i.e. with more than 8 per cent MgO do not have the same hydraulic value as slags poor in magnesia but of comparable composition. According to established finding of Stutterheim and Nurse²⁴ in slags with 15 per cent to 18 per cent MgO, it appears, that the MgO possesses no hydraulic value in such high contents. Datt²⁵ has reported that higher amounts of MgO in the slag from which blast-furnace slag cement is made may slow down the rate of hardening slightly.

In order to find out the most favourable chemical composition of the slag, taking into account the effect of major oxide constituents of slag, the compressive strength tests on glasses within the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system with 5 per cent MgO added were carried out by Locher²⁶. The glasses were mixed with Portland cement and gypsum in the proportions 77:18:5 by weight and the tests made on cement mortars according to the German standard (DIN 1164). The most favourable composition of glass was 50 per cent CaO, 31 per cent SiO_2 and 19 per cent Al_2O_3 . A similar composition proved most favourable for activation with other activators also. Broadly similar results were obtained by Tanaka²⁷ and by Solacolu²⁸. Tanaka found the optimum glass composition for Portland cement clinker

activation as 51.5 per cent CaO, 33 per cent SiO₂ and 15.5 per cent Al₂O₃. For anhydrite activation the optimum composition was 49-50 per cent CaO, 31-33 per cent SiO₂ and 18-19 per cent Al₂O₃.

While these results give a general picture of the influence of slag composition on reactivity, it is not a complete one since the amount and kind of activation that gives maximum strength varies with the composition of the slag. Tanaka found that in supersulfated cements Portland cement clinker that gave maximum strength varied from 2 to 6 per cent with different slags. The action of lime as an activator also seems to differ from that of Portland cement or calcium sulfate. This has been attributed by Locher to differences in the hydration products and the strength they develop. It is evident that there are many factors influencing strength development which have yet to be fully worked out.

2.2.6 Chemical Composition Requirements:

Attempts have been made to reproduce the complicated relationship between the chemical composition and hydraulic properties in formulae. The formulae³ which are given below have been evolved from experience and

from tests on the strength of granulated slag mixes, are for the compositions desirable in the slag. In the absence of any quantitative theory for the relationship between and the activity and composition of granulated slag, such formulae are at most useful working rules, but these rules are obviously needed as a guide in the production⁴ of slags.

In Germany the formula first adopted for granulated slags to be ground with Portland cement required that the ratio of the percentage contents of the oxides should be:

$$\text{FI : } \frac{\text{CaO} + \text{MgO} + \frac{1}{3} \text{Al}_2\text{O}_3}{\text{SiO}_2 + \frac{2}{3} \text{Al}_2\text{O}_3} \geq 1$$

This was superseded in 1942 by the formula which still appears in the specification DIN 1164:1967 :

$$\text{FII : } \frac{\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2} \geq 1$$

In order to enable a more accurate distinction to be made between very good, good and suitable slags, formula III was proposed:

$$\text{FIII: } \frac{\text{CaO} + \text{CaS} + \frac{1}{2} \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2 + \text{MnO}} \approx 1.5$$

Hydraulic Properties

medium	good	very good
< 1.5	1.5 - 1.9	> 1.9

The essential difference in these three formulae is the transfer of Al_2O_3 in its full amount to the numerator and the consideration of S and MnO. According to Keil⁸ excellent results are obtained in judging the slags on the basis of Formula III. The FIII value only refers to the glassy constituents soluble in HCl. In India formula I is taken as the standard.

There are, of course, many shortcomings in formulae of this kind, but they enable a quick evaluation to be made when the chemical composition of the slag is known, which is the case at every blastfurnace works.

From statistical correlations of various formulae with the strength of a wide range of British granulated slags mixed with Portland cement, Parker and Nurse concluded that the German Formula I gave the best correlation when combined with a measure of the percentage of glass in the slag. The product GM, where G is

the percentage of glass and M the Formula I, was accordingly proposed as a guide to the activity of a slag. The higher the value of GM the more hydraulic is the slag provided that M has a value between 0.72 and 1.5. At lower values of M the slag has no hydraulic activity and above 1.5 the slag cannot be granulated without devitrification occurring. The adoption of Formula I implies that MgO is as effective as CaO in producing hydraulic properties in a slag, but the slags on which the product GM was tested only covered samples with a MgO content upto 7.5 per cent.

DeLangavant²⁹ considered the following formula as being particularly suitable as an 'index of quality' which is somewhat simpler from the German Formula III:

$$i = 2\theta + CaO + Al_2O_3 + 0.5 MgO - 2 SiO_2$$

DeLangavant classifies the hydraulic properties of slags as inferior if $i < 12$ and very good > 16 ; but Blondiau³⁰ has put the minimum desirable value at 19 for slags of low (3.5 per cent) MgO content.

Blondiau³¹ from tests on Belgian slags, in both slag-Portland and supersulfated type cement, found that most reliable results were obtained with slags with a $CaO:SiO_2$ ratio between 1.45 and 1.54, a $SiO_2:Al_2O_3$ ratio

between 1.8 and 1.9 and a 'hydraulic potential' between 70 and 80 cal/gm. The latter is a measure of the degree of vitrification.

2.2.7 Methods of Evaluating Hydraulic Properties of Slag:

In order to permit a rapid evaluation of the hydraulic properties without knowledge of the chemical composition, a number of methods are available in literature. Although these methods have not yet found general application, they render good service in special cases.

Considerable use is made in Germany of a fluorescence test² as a rapid method for assessing granulated slags. However, the experience with British slags indicate that this test is useful only for slags produced by one particular process or even by a single furnace. In this test the sample is examined under ultraviolet light. Vitreous slag particles are claimed to emit red and pink colours whereas highly crystalline particles emit blue and violet colours. The product of the percentage of red fluorescing particles in a granulated slag multiplied by the $\text{CaO}:\text{SiO}_2$ ratio of the slag is considered to be a reliable index of hydraulic value. It is evident from this test, and that used by Parker and Nurse, that neither a composition formula nor a glass

content alone are sufficient to characterize the hydraulic properties of a slag and that some product of the two is required.

Mussnug³² has carried out a quick test of mixes of finely ground slags with various activators by heating them with steam. In this test, cylindrical specimens of low hydraulic slags attained less than 100 Kg/cm^2 compressive strength, high hydraulic slags more than 200 Kg/cm^2 . This method provides useful values, particularly if it is desired to use the slag sands for the production of steam-hardened metallurgical bricks.

An indication of the hydraulic value of a slag can be obtained with the microscope if the refractive indices are determined. The refractive index of slag glasses varies from about 1.635 to 1.67, but lime rich slags usually have an index above 1.65.

According to Gille's³³ method which is an improved version of the method used by Guttman and Weise³⁴, 0.5 gm of slag of 0.06 to 0.09 mm grain size is heated in a test glass after addition of 12 ml. of potassium hydroxide in a container of water upto the boiling point of the water. The filtered slag is shaken with 5 ml. of a 0.5 per cent methylene blue solution, and filtered off and dried. The resulting colouring is slight in low

hydraulic slags as compared to higher hydraulic slags but does not run parallel with the strengths.

A chemical method for assessing the activity of granulated slags have been described by Lieber³⁵. 5 gm of the slag ground to a specific surface of $3200 \text{ cm}^2/\text{gm}$ is snaken for 3 hours at 80°C with 50 ml 5 per cent NaOH solution, filtered, washed, four times with 40 ml methanol and twice with 25 ml diethyle ether. The residue is then dried for 30 minutes at 60°C and the loss on ignition at 600°C is determined as a measure of the bound water. A fair relation was found between the amount of bound water and the strength developed in a 50/50 Portland cement-slag cement tested in German Standard mortars (DIN 1164). A further microscopic method has been applied by Ihonelsen³⁶. He mixes finely powdered slag with a drop of 2 per cent aluminium sulfate solution, and observes when the first needle formation occurs and when the crystals are completely developed. In high hydraulic slags, needle formation occurs within one minute, in low hydraulic slags only after four to five minutes. In the first case, crystal formation is completed after 5 minutes, whereas in the second, it takes upto 35 minutes. This test, in itself a sensitive one, reacts to devitrified slags, however, just as quickly as to glassy slags, and thus

gives no reliable indication of the hydraulic value of a slag. This method proved to be impracticable for quantitative purposes and cannot be applied to crystallized slags.

Bloindau proposed to determine the 'hydraulic potential' as the difference in the heat of solution of an untreated powdered slag and one heated for four hours at 1000°C with a specific surface of approximately 4860 Sq.cm/gm according to Blaine. He found that the release of devitrification heat is greatest at 1000°C and reaches its maximum value as quickly as $1\frac{1}{2}$ hours. On the basis of these findings he postulated that slags are assuredly suitable for production of cement, as mentioned earlier also, when hydraulic potential lies between 70 and 80 cal. per gram.

Passow³⁷ has indicated that testing with sodium or potassium hydroxide leads readily to measurable and comparable strengths. Relying on thorough experimentation, Feret³⁸ recommended the making of cubes from 1 part slag and 2 parts standard sand which are mixed with 11 per cent of NaOH solution and hardened for 24 hours at a constant temperature. The strength values thus obtained tally well with those after normal heating. Feret considers this method to be particularly useful as

it supplies usable values quickly, and because the properties of the slag are not concealed by the addition of other binding agents.

Composition formulae given before are convenient for the rapid control of slag quality since regular chemical analysis of slag is anyway carried out for the control of pig-iron production. However, the final guide is the strength developed in cements. For the purpose of assessing the contribution to strength made by the slag a 'hydraulic index' is recommended by Keil⁸. This is based on a comparison of the compressive strength at 28 days of mortars containing (1) the Portland-slag cement, (2) the same Portland cement alone, and (3) a Portland-ground quartz sand cement (sand ground to a specific surface of 4000 cm²/gm by air permeability method. If the strength developed in mortars 1, 2 and 3 are a, b and c respectively, and the amount by weight of slag, or ground quartz, in cement 1 and 3 is 30 per cent, then

$$\text{Hydraulic Index } 70/30 = \frac{a - c}{b - c} \times 100$$

If the slag is non-hydraulic its effect should be similar to the inert ground sand and the hydraulic index be zero. If it is as cementitious as the Portland

cement itself the index should be 100. In practice the index is found to vary with the proportion of slag present in the cement and it is not necessarily the same in a 50/50 or 30/70 Portland cement-slag mix as in the 70/30 mix. This test though takes time, gives fairly reliable results.

2.3 Slag Cements

Various types of cements which use slag as one of the ingredients are described below.

2.3.1 Lime Slag Cement:

Cements made of mixtures of hydrated lime and ground granulated slag were the earliest of cementitious products made from slag. The use of this cement has, in fact, now practically died out in most countries, although some, notably France and Belgium, still retain standard specifications for the material which is used as a masonry cement. In Great Britain the cement was known as slag-cement, or 'Gold Process Cement'; in the United States in the early years of the present century it was sometimes known by the confusing name of pozzolan cement. It is now known there as 'Slag Cement' and is defined as a mix

consisting essentially of granulated slag and hydrated lime containing at least 60 per cent slag.

According to Feret³⁸ with the normal granulated slag of high-lime content, about 10 per cent of high calcium lime is required to give optimum results. Hydraulic lime may be used instead of high calcium lime without affecting the strength, but a higher content of lime is needed. In practice, higher lime contents upto 30 per cent, are used to offset the deleterious effects of carbonation during storage which can render the cement inactive. As the slag-lime mix sets rather slowly, an addition of sodium sulfate to the extent of 1 per cent or less was sometimes made, but it had the disadvantage of producing efflorescence. A gypsum addition can be made with advantage instead of sodium sulfate. Slag cement specimens after storing in water show a strong greenish tint when fractured and the odour of H_2S can often be detected.

Different countries prescribe different specifications for the amount of lime in slag cement depending upon the type of slag available in the country. Although slag is considered as a latent cement where lime functions as an activator, it has been reported by various workers that some lime is absorbed during hydration. It is,

therefore, expected that the quantity of lime in the lime-slag mixes will have definite influence on slag hydraulicity.

Samaddar and Lahiri¹⁹ on the basis of tests done on lime-slag cement concluded that

- (i) the compressive strength increases with lime content in slag and with increase in proportion of added lime upto a certain limit and also with increase of basicity of the slag. Effect of added lime is more pronounced when the CaO content of the slag is less.
- (ii) lime required for the development of maximum strength increases as the basicity of the slag decreases.

These conclusions seem to be related to the absorption of lime by slag during hydration which depends upon CaO content and also on hydraulicity of the slag which increases for slags of the same CaO content with increase of Al_2O_3 content. The lower the CaO content and higher the Al_2O_3 content of the slag greater is the absorption. The greater increase in strength with increase of lime for slag poor in CaO may be due to the fact that in mixtures low in lime content, lime required for activation is not sufficient, the amount being so small that it is absorbed during the earlier period of setting and

hardening. Results therefore indicate that for proper activation of slag poor in lime a proportionately larger amount of lime should be present in lime slag mixture.

Lime-slag cements have been specially used for sea water and underground foundation works because of their resistance to attack by sulfates and because of their good plasticity.

The abandonment of production of this form of cement in most countries must be ascribed to its sensitivity to deterioration in storage and its low strength in comparison with modern Portland cements.

2.3.2 Slag as a Raw Material for the Manufacture of Portland Cement Clinker:

A slag containing 30-35 per cent lime, 30-40 per cent silica, 10-18 per cent alumina and small amounts of magnesia, and oxides of manganese and iron is, except for its lower lime content, similar in composition to Portland cement. If mixed with necessary quantity of limestone its composition can be brought to that required in a Portland raw mix. Blastfurnace slag forms, therefore, a very useful raw material for the manufacture of Portland cement.

The slag and limestone are finely ground and mixed in the requisite proportions and burnt in a rotary kiln in the usual manner. The resultant clinker often has a somewhat brownish colour, owing to the manganese oxide present, but does not differ in any other respect from the clinker obtained from a clay or shale raw mix. High lime slags are usually preferred since a smaller addition of lime is required in preparing the raw mix. The fuel consumption is somewhat reduced by the slag-limestone mix since a smaller amount of calcium carbonate has to be dissociated during burning.

Air-cooled lump slag is sometimes used but it is more common to employ granulated slags. The dry process of cement manufacture is most often used, but some plants utilize the wet process also, which avoids the necessity of drying the slag. One difficulty which is peculiar to this raw material is encountered in the manufacture of Portland cement by the wet process from blastfurnace slag. A slurry containing a ground high-lime blastfurnace slag has a definite tendency to thicken and gradually set into a cake. This is due to the latent cementitious properties of the slag which thus exhibit themselves in a slight degree without the presence of any accelerator. The tendency of setting of the slurry is more marked with

granulated slag than with the air-cooled slag. The setting action increases rapidly with temperature and at about 36°C may become very rapid. This trouble has been surmounted by the addition of a small amount of sugar which inhibits the setting of slurry and by storing the slurry for as short a time as possible before use.

2.3.3 Portland Blastfurnace Cement:

Portland blastfurnace cement is produced by mixing slag with Portland cement. British standard exists for two forms: Portland blastfurnace cement less than 65% slag (BS: 146-1968) and low heat Portland blastfurnace cement 50-90 per cent slag (BS 246-1968). In the U.S.A.; where the cement is called Portland blastfurnace slag cement, the granulated slag content is from 25 to 65 per cent ASTM (595-1968). The proportion of cement to slag varies with different product, the practice in different countries being given elsewhere³⁹.

Though it has been usual to grind the Portland cement clinker and the slag together they may be separately ground and subsequently mixed⁴ at the site to produce onsite Portland blastfurnace type cement. When ground together it is the softer material, the clinker which will be preferentially ground. With upto 50-60

per cent slags, the early strength is mainly determined by the fineness of the clinker fraction and later strengths by that of the slag fraction. With cements of higher slag content the fineness of the slag is of major importance at all ages.

The cement clinker used in the manufacture of Portland blastfurnace cement is required to conform to the same composition limits as are laid down for Portland cement alone and according to Atwell⁴⁰ slag to be used in Portland blastfurnace cement should conform to the formula

$$\frac{\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3}{\text{SO}_2} = 2 \text{ (good slag)}$$

Usually slags with high lime content are preferred for Portland blastfurnace cements.

Portland blastfurnace cement is similar in physical properties to ordinary Portland cement and the standards for the two are identical in respect of fineness, setting time and soundness. The rate of strength gain is somewhat lower than for Portland cement. Portland blastfurnace cement therefore tends to be weaker at early ages than ordinary Portland cement but at an age of one or two years it may be equally strong or even a little stronger. Atwell⁴⁰ and Taylor⁴¹ on the basis of

laboratory tests on Portland blastfurnace cement concluded that

- (i) the strength of Portland blastfurnace cement at any particular age during the early life is less than the strength of the cement containing none of the granulated slag.
- (ii) at constant water/cement ratio the reduction in strength compared with the 100 per cent ordinary Portland cement increased with increasing slag replacement, but the reduction decreased with age.
- (iii) the 28 day compressive strength of concrete containing no granulated slag was achieved within three months by concretes containing upto 40 per cent of the granulated slag. With upto 50-70 per cent slag the time required to reach 28 day reference strength might well be one year or more.
- (iv) the usual water/cement ratio to strength relationship found with Portland cement concrete holds good for concretes containing granulated slag.

Atwell has also postulated and verified the equation which relates the change in strength by slag addition to water/cement ratio and degree of replacement. It is known that for Portland cement, in the range of medium level cube strength, a linear relation exists in the form

$$U_c = A \frac{C}{W} + B \quad \dots \dots (1)$$

where, $\frac{C}{W}$ is cement/water ratio. A is determined largely by the characteristics of the cement, and the intercept B by the curing period and the type of aggregate. A postulate follows for slag replacements, that with the same effective water content

$$U_{c+s} = A \frac{C'}{W} + B + D \frac{S}{W} \quad \dots \dots (2)$$

where, $\frac{S}{W}$ is slag to water ratio by volume, and

$$C = C' + S = C' + K'C$$

K' being the slag replacement proportion by volume. D is the slag characteristic for strength and, apart from being affected by chemical composition and fineness of slag and the cement is like, B, dependent on maturity.

The change in strength between relationship (1) and (2) becomes

$$U_c - U_{c+s} = K' \frac{C}{W} (A - D) \quad \dots \dots (3)$$

which indicates that reduction in strength is directly proportional to the $\frac{C}{W}$ ratio and degree of replacement.

This postulate has been found by the workers to give better correlations at later ages than at early maturity.

It has also been found by laboratory tests that at constant water, the workability of the mix increases with increasing granulated slag content. Thus if the workability of the mix is to be kept constant, the addition of slag must be compensated for by reduction in free water content of the mix. This will reduce the effective water/cement ratio of the mix which will lead to an increase in strength properties.

The heat evolution during the setting and hardening of Portland blastfurnace is lower than that of Portland cement. This property of Portland blastfurnace cement can be used to advantage in mass concrete structures to reduce the temperature rise but it is a disadvantage in cold weather where the rate of hardening may become very slow. The effect of low temperatures in retarding the strength development of Portland blastfurnace cement seems to be comparable to that of Portland cement when the water:cement ratio of the cement is low⁴² (0.4). At $\frac{W}{C}$ ratio of 0.5 and more,⁴³ the blastfurnace cement is more affected. The loss in strength at low temperatures is also more pronounced in cements with slag contents approaching or above 70 per cent.

Portland blastfurnace cement is slightly more resistant to sulfates or slightly acidic waters than ordinary Portland cement and is often specified for marine work. The moisture movement, drying shrinkage and creep of this cement are very similar to those of Portland cement as is also the bond to steel reinforcement.

In India Associated Cement Companies produce this type of cement. In Belgium a modification of the usual process for making Portland blastfurnace cement is used and the process is known as Trif Process. In this process the slag, after granulating, is ground wet and stored as a wet slurry. It is kept as a separate constituent until the concrete is being mixed in the concrete mixer where the Portland cement, slag slurry and aggregate are added together. The advantages claimed are saving in fuel for drying the slag and a greater efficiency of grinding in the wet state.

In France, fly ash is also added in some proportions to the Portland blastfurnace cement and the product is known by a special name of Ternary cement. It is stated that it meets the strength requirements for ordinary Portland cement and offer particular advantages in workability and chemical resistance.

2.3.4 Hydration of Portland Blastfurnace Cement:

The hydration of Portland cement-granulated slag mixes is more complex than that of Portland cement, since both constituents react with water. There seems little doubt that the Portland cement grains hydrate in the usual manner i.e. C_3C and C_2S converting to calcium silicate hydrate gels, C_3A and C_4AF to sulfoaluminates, calcium aluminates and sulfoferrite hydrates and some Al_2O_3 as well as Fe_2O_3 and SiO_2 entering into a hydrogarnet phase. We have, therefore, to consider the hydration of the slag as influenced by the calcium hydroxide liberated from the Portland cement. No hydration products can be observed when ground granulated slag is placed in water. This is ascribed to the formation of acidic surface films as a small amount of Ca^{++} ions is released into the solution. In a calcium hydroxide solution reaction occurs which removes this film and thus hydration continues as the lime breaks into the silica framework of the slag.

Production of amorphous matter from both slag and cement grains can be observed within a few hours after mixing water to Portland blastfurnace cement. After a day large numbers of plates and needles of hydrated calcium aluminate, and large columnar crystals of calcium hydroxide can be seen.

The hydration products clearly identified⁴ in set blastfurnace cement are:

1. A tobermorite*-like calcium silicate hydrate phase which probably contains alumina in solid solution for not all the alumina can be accounted for in the other hydration products. This phase may also contain magnesia in solid solution because free $Mg(OH)_2$ cannot be detected in the set cement.
2. Hexagonal tetracalcium aluminate hydrate or its solid solution, or intergrowth, with $3CaO(Al_2O_3, Fe_2O_3).CaSO_4.12H_2O$.
3. An ettringite-type phase $3CaO(Al_2O_3, Fe_2O_3).3CaSO_4.31H_2O$.
4. Calcium hydroxide.

The relative extent to which the tri- and mono-forms of calcium sulfoaluminates are formed in the early stages of hydration is considered by Ludwig to depend on the reaction velocity of the alumina compounds and the rate of solution of the calcium sulfate retarder. An increase in the former favours the formation of the mono-compound.

* Formula of tobermorite gel is $5CaO.6SiO_2.XH_2O$ where X varies from 1 to 9.

The extent to which calcium hydroxide is present will vary with the Portland cement: slag ratio in the cement. In mixes of low Portland cement content it may be absent in the later stages of hydration. Other compounds that might sometimes be formed are hydrated gehlenite (C_2ASH_8) and hydrogarnet. Locher⁴⁴ found both these compounds in the hydration products of $CaO - Al_2O_3 - SiO_2$ glasses and that the C_2ASH_8 subsequently took up more lime to transform into a hydrogarnet of about C_3ASH_4 composition. However, Smolozky⁴⁵ in the examination of a large number of set blast-furnace cement was only able to identify C_2ASH_8 in one case, and a hydrogarnet in another case after a year's storage in water. Similarly, Sersale⁴⁶ did not find any hydrated gehlenite in set cements stored for a year or more in water. It seems that in cements these two compounds can at most be only minor hydration products. Another product that may occur rarely is C_2AH_3 .

Having discussed lime-slag and Portland blast-furnace slag type cements we next come to the last but the most promising cement, the supersulfated cement, made from slag.

2.3.5 Supersulfated Cement:

This cement is made by activation of the granulated blastfurnace slag by means of calcium sulfate. Its properties are liable to be variable according to the materials available to the manufacturer and, in particular, to the reactivity of the slag.

The cement is made by grinding a mixture of 80-85 per cent granulated slag, 10-15 per cent anhydrite or hard burnt gypsum, and about 5 per cent Portland cement, the product is ground more finely than is the characteristics of Portland cement. Different standards put different limits on the amount of slag, MgO and SO_3 content in the cement for maximum strength depending upon the slag composition.

As D'Aris and Eick⁴⁷ have shown that usually a moderately high lime and alumina content is preferred in the slag used in making these cements. Keil gives values of 10-15 per cent alumina but cements are made satisfactorily with slags of rather lower alumina content. Keil and Gille⁴⁸ recommended a modulus of at least 1.8 and preferably 1.9 or higher as calculated by the formula III on page 31.

Indian slags which are characterized by low $CaO - SiO_2$ and $SiO_2 - Al_2O_3$ ratio, as such are not considered suitable for making supersulfated cement. But

Chopra and Kishanlal⁴⁹ have shown that in the light of the observations made by Keil and Locher and by Blondiau regarding the quantity and solubility of CaSO_4 in relation to the contents of lime and soluble silica, the strength could be raised substantially by carefully working out the optimum conditions of activation so as to make the Indian slags suitable for commercial exploitation. They observed that, for the slag used, maximum strength was obtained by a mix containing 70 per cent slag, 25 per cent gypsum and 5 per cent Portland cement.

Supersulfated cement has a specific gravity of approximately 2.9. It is said to be made from 'False Set' and its initial setting time varies between $2\frac{1}{2}$ hours and 4 hours and its final setting time between $4\frac{1}{2}$ hours and 7 hours.

One of its most important properties is its low total heat of hydration which amounts to only approximately 38 calories per gram at 7 days and 42 calories per gram at 28 days. It is therefore very suitable for the construction of dams and all mass concrete work but requires greater care when concreting in cold weather. Concrete made with supersulfate cement may expand or contract slightly on setting according to conditions. Shrinkage is due to the drying out of water and the expansion is due to

crystallization on hydration of certain of the constituents. In general it appears that a small shrinkage will take place if the concrete is cured in air, and a small expansion, if cured in water. Subsequent drying shrinkage is about the same as for Portland cement. It has about the same permeability as Portland cement concrete.

Supersulfated cement, like high-alumina cement, combines with more water on hydration than does Portland cement. The strength falls off more rapidly than with other cements as the aggregate content of the mix is increased, so that it is not desirable to use mixes much leaner than 1:2:4. The cement is rather more sensitive to deterioration during storage than Portland cement owing to the effects of carbonation; the setting time is lengthened and the early strength is affected seriously. Cement that has deteriorated in this way can be restored by the addition of 1 per cent hydrated lime.

The rate of hardening of this cement increases with temperature up to about 40°C. At higher temperatures the strength drops and a similar effect is found on curing in high pressure steam. Under normal curing conditions standard 1:3 mortar cubes show compressive strength which is liable to be less than that of the cubes made with rapid hardening Portland cement at early age but is

comparable or better than the corresponding values for rapid hardening Portland cement at 3 days and greater ages. The same tendency is indicated with cement cubes. The development of strength depends principally on the type of slag used in its manufacture and if a particularly good slag is available strength nearly as high as those of high alumina cement concrete are obtainable at both early and greater ages.

Tanaka's²⁷ studies on supersulfated cement have shown that it possesses low surface abrasion quality. There is no direct relationship between compressive strength and surface hardening of these binders. Abrasion resistivity is improved the higher the CaO contents, the lower the Al_2O_3 content of the slags. The low surface hardness was further tentatively explained by Yamachi et al⁵⁰ as due to an action of CO_2 absorbed from the atmosphere which lowers the pH of the liquid phase in the setting cement and thus disturbs the surface hydration reactions during hardening. To a certain degree it is possible to overcome this troublesome phenomenon by preparing the cement mix with a higher degree of basicity and finer size, keeping the water/cement factor low, and curing in lime water in place of common water, followed by air curing in an atmosphere of high humidity.

A big advantage of supersulfate cement is its comparatively high resistance to chemical attack and it was probably for this purpose that it was originally developed. Blondiau⁵¹ found a satisfactory behaviour during test periods of up to 3 years in contact with natural ground waters strongly sulfated, MgSO_4 , $\text{Al}_2(\text{SO}_4)_3$ and $(\text{NH}_4)_2\text{SO}_4$ solutions, humic acid in the presence of MgSO_4 and NaCl , and artificial and natural sea water. Good resistance was also shown against HCl and also to linseed oil, an agent which damages both Portland cement and Portland blastfurnace slag cement.

The cement is also resistant to weak concentrations of organic acids (e.g. below 0.5 per cent) such as lactic, acetic, citric and tartaric acids and phenols and cresols. Stronger solutions such as 1 per cent cause damage⁵². Chlorides and alkali hydroxides and carbonates seem to have no action.

Supersulfated cement has been used in, harbour and break water constructions, chemical works under conditions involving exposure to high concentrations of sulfates and for the underside of bridges over railways to resist the action of locomotive flue gases.

2.3.6 Hydration of Supersulfated Cement:

The initial setting and hardening of supersulfated cement is associated with the formation of calcium sulfoaluminate from the slag constituents and added calcium sulfate.

The formation of the high sulfate form of calcium sulfoaluminate (ettringite) does not take place readily in saturated lime solution and the monosulfate tends to be formed as an unstable phase; neither can ettringite be formed in water with no calcium hydroxide present. The Portland cement addition to the cement is required to give correct alkalinity to enable the ettringite to be formed.

Blondiau found the most favourable concentration to be about 0.2 gm CaO per litre in the liquid and later workers⁵³ indicate a range from 0.15 to 0.59 gm CaO per litre. Combination of lime by carbonation leads to a low CaO concentration in the solution and this accounts for its deleterious effect. An excessive addition of Portland cement giving a saturated lime solution results in low strength. In manufacture, hydrated lime can be used in a smaller proportion in place of Portland cement but the latter is rather less sensitive to carbonation and is, therefore, preferred.

Examination of the set cement by X-ray and DTA methods has shown that the main hydration products are ettringite and tobermorite-like phases⁵⁴. The early strength seems to be largely attributable to ettringite formation, but the development of strength from about three days onwards must come from the increasing formation of calcium-silicate hydrate. There is less certainty about the extent to which, and at what stage, the monosulfate form of calcium sulfoaluminate is produced. Blondiau⁵⁵ had earlier suggested that it was formed during the first few hours when the CaO concentration in the solution was high, and that as the lime in solution became depleted by this reaction, the reserves being small, the formation of ettringite set in. It has not been detected at this stage but Smolazyk was able to identify it in the set cement at seven days. Whether it is formed directly, or by decomposition of ettringite as D'Ans and Eick⁵⁶ suggested, is still not clear, though it may be questioned if a change between two compounds of such different molecular volume could occur without some marked effect on strength.

The amount of SO_3 in supersulfated cement is sufficient only for conversion of about a quarter of the alumina to ettringite, so the excess must be present in other forms, hydrated or unhydrated. Even the formation of

monosulfate still leaves substantial excess of alumina. From consideration of the phase equilibrium in the system $\text{CaO} - \text{Al}_2\text{O}_3 - \text{CaSO}_4 - \text{H}_2\text{O}$, D'Ansand Eick deduced that hydrated alumina must be a product of the hydration and considered that the final product is a mixture of the two forms of calcium sulfoaluminate and hydrated alumina together with hydrated calcium silicate. The hydrated alumina has not been detected by X-rays but it would be expected to be amorphous. Some of this missing alumina is probably present in the calcium-silicate hydrate phase. The ettringite formed is probably not the pure compound. Firstly ferric oxide may substitute for alumina and, secondly, Nurse has advanced evidence that the phase in supersulfated cement contains some $\text{Ca}(\text{OH})_2$ substituting for CaSO_4 .

2.4 Effect of Temperature on Cement Properties

Hydraulic cements have been used for making heat or fire resistant concrete. The main constituent materials of refractory concrete are the binding agent and the aggregate, the latter usually being fire resistant. Both play an important role in determining the properties of a refractory concrete.

If a cement structure is subjected to heat after it has set, it loses its adsorbed and entrained water in certain ranges of temperature and after passing through an intermediate water free state, finally reaches a stage where new phases are built-up.

Strain shrinkage phenomena are of particular importance in regard to the first heating of refractory concrete when they are brought into service and the subsequent first cooling down. The binding agents undergo an irreversible volumetric change when they are first heated up. Investigations on Portland cement show a similar picture, a number of different workers agree on a value of shrinkage of about 1.5 per cent up to 900°C . Cooling to room temperature causes a further contraction so that the total change in length after first heating cycle has a value of about -2.4 per cent. After the first heating process, the cement structure exhibits a reversible expansion with temperature of approximately 1% at 1000°C . In refractory concretes the expansion processes are rather more complicated because during the first heating the expansion of the refractory aggregate is superimposed upon a shrinkage of the binding agent constituent. It will be evident that the total shrinkage of approximately 2 per cent referred to above will not appear in concretes, since

cement contents are of the order of 15 to 25 per cent of the total mass of the concrete. The shrinkage effects are therefore decisively reduced and may even disappear altogether. Refractory concrete, like pure cements, expand like other materials, once they have been subjected to their first heating.

The heating of cements to temperature in the middle to high range (400-1000°C) results in noticeable deterioration of the strength due to disintegrating reactions and the associated phase building. This fact is the reason for the critical strength of refractory concrete which can extend over a varying region of temperature scale depending upon the type of cement, the additives and so on until a point is reached at which there is a renewed increase in strength caused by ceramic binding. Compressive strength curves against temperature, for various cements are given elsewhere⁵⁷.

Blastfurnace slag cements have also been used for the production of refractory concrete. An important fact which influences the behaviour of refractory concrete is that, no or very little, free Ca(OH)_2 should occur during hydration. When the temperature is raised to 500°C or above, the Ca(OH)_2 present loses its combined water and changes into very reactive CaO . It is only to be expected

the physical state of the slag its chemical composition which, except the lime content, is quite similar to Portland cement composition plays an important role in determining the hydraulic value of the slag.

Oxides like CaO and Al_2O_3 up to certain limits seem to improve the hydraulicity whereas no firm view exists on the effect of magnesium oxide. Different workers have expressed different opinions about its effect, however, from the literature surveyed it can be inferred that high content of magnesia if not present in the form of periclase is not detrimental to strength except that it might slow down hydration process. SiO_2 which is an acidic oxide reduces the hydraulic value. Mineralogical composition of the slag in equilibrium though tried for predicting hydraulicity does not give reliable correlation.

In general, in all types of slag cements, slags with higher CaO and relatively high Al_2O_3 are preferred but to give a slag composition that will give best results under all conditions of activation is very difficult because the activating mechanism of each activator differs from that of other.

Various experimental methods have been suggested for determining the hydraulic value of the slag but to have a reliable information it is better to perform actual strength tests. Out of number of slag cements produced supersulfated cement seems quite promising.

CHAPTER 3EXPERIMENTAL PROCEDURE RESULTS AND DISCUSSION3.1 Experimental Procedure

3.1.1 Slag:

Granulated slag used in the study was obtained from TISCO and it had the chemical composition as given in Table 3.1.

Table 3.1
Chemical composition of TISCO blastfurnace slag

Oxide	Wt %
SiO_2	32.0
Al_2O_3	28.0
CaO	32.9
MgO	4.6
MnO	1.6
FeO	0.7

In the light of the formulae mentioned for hydraulic behaviour of slag in Chapter 2 it was found through chemical analysis that the slag was not of very good quality and in fact ratios CaO/SiO_2 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ were quite below the prescribed limits.

3.1.2 Grinding and Mixing:

Granulated slag used in making cement was ground in laboratory ball mill of size 10 litre for 6 hours with alumina cylinders of 1 in. length and $\frac{3}{4}$ in. diameter as the grinding media. Ratio of the charge to amount of alumina cylinders in the mill was kept at 1:3 by weight. This was fixed after doing some preliminary tests on grinding efficiency of the mill to determine the ratio which gave best result. Fineness of slag after 6 hours of grinding was 4097 Sq.cm./gm. as measured by Blaine's air permeability apparatus in accordance with the procedure given in IS 4031-(1968).

Different activators were mixed in the slag to give different cements. To ensure better and thorough mixing of an activator in the slag these two were tumbled in a ball mill. A few alumina cylinders were also added to the ball mill charge to avoid the agglomeration and sticking of the fine powder to the mill's surface.

3.1.3 Strength Tests:

For testing of cements, compressive strength tests were carried out on 1:3 mortars after one, two, three, four and twelve weeks water curing. Standard mortar cubes were made according to Indian specifications in IS 4031-(1968), using standard Ennore sand which conformed to IS 650-(1966) except that it passed through 850 micron IS sieve and not more than 10 per cent by weight passed through 600 micron IS sieve.

Standard consistency of the cement pastes was determined by Vicat's needle as per IS 4031-(1968) and the amount of water for making cubes was calculated by the formula $(\frac{P}{4} + 3.5)$ per cent where P denotes the standard consistency as determined above. Cubes were cast in brass moulds of 50 cm² face area, using tamping rod for compaction. These moulds were kept in moist air of at least 90 per cent relative humidity and at a temperature of 27° ± 2°C for 24 hours and then demoulded and immersed in water for subsequent curing.

The compressive strength tests were carried out on a RIEHLE compression testing machine by applying load at a rate of approximately 350 Kg/Sq.cm/min. For each strength test at least three cubes were tested and the average value was recorded.

Initial and final setting times for various cements were also determined following the procedure prescribed in IS 4031-(1968).

Concrete cubes (15 x 15 x 15 cu.cm.) were cast as per IS 516-(1959) specifications, using supersulfated cement, standard sand, and aggregate (50 per cent 40 mm size and 50 per cent 20 mm size) in the proportions 1:2:4. These concrete cubes were cured in the same way as done for mortar cubes, and tested for compressive strength after different periods of curing. The testing load was applied at a rate of 140 Kg/Sq.cm./min. and for each test three cubes were tested, and the average value was recorded.

3.1.4 X-Ray and DTA Analysis:

X-ray examination was done on hydrated samples to determine the phases formed on hydration. X-ray diffractographs were also obtained for pure ground granulated slag and unhydrated cement for comparison with the hydrated cement diffractographs.

Samples for X-ray analysis were prepared by making cement pellets with water/cement ratio of 0.5. These pellets, after one day's moist air curing, were immersed in water for 7 and 28 days respectively. Cured samples (dried) were ground to a fineness of 200 mesh and filled

in a standard sample holder. After filling the powder in sample holder its surface was gently pressed and levelled using a flat glass plate. The powder did not require any binding agent as the powder compact was strong enough to bear small shocks. Radiation used in the examination was CuK_α and the receiving slit angle was 0.2° . The tube was operated at 35 KV and current was 20 mA. The time constant was kept at 4 and the counter was operated at 1000 cps. The sample was rotated at an angular speed of 2° per minute and the chart moved with a speed of 1 in. per minute. Range of 2θ angle scanned was from 8° to 55° .

Differential thermal analysis of the unhydrated as well as of hydrated cements was done using a 'MOM DERIVETOGRAPH'. Samples were subjected to temperatures ranging from room temperature to 1000°C . Rate of increase of temperature was kept at $10^\circ\text{C}/\text{minute}$. Platinum-platinum/rhodium thermocouple and $\alpha\text{Al}_2\text{O}_3$ reference material were used in the investigation.

3.1.5 Tests at High Temperatures:

High temperature testing of supersulfated cements was carried out on cylindrical pellets of 4.58 cm. in diameter and heights varying in the range between 2 cm. to

4 cm. These pellets were made in Carver's laboratory press by applying a load of 4550 Kg. composition used consisted of 1 part of cement and 4 parts of fire brick grog (by weight) which had particle size distribution -12 and +14 mesh ASTM sieves. Water/cement ratio was kept at 0.6. Water content was chosen in such a way that it was sufficient to form a lump when the mix was squeezed by hand but it did not flow out of the gaps between the die and the plunger when the mix was pressed in the die. While making the pellets, tray containing the mix was covered with a wet cloth to avoid drying of the mixture by evaporation of water. Pellets were allowed to dry in moist air of controlled humidity for 24 hours and then submerged in water for subsequent curing. After 7 days curing specimens were taken out and in order to determine strength as a function of temperature, heat treated for 16 hours at different temperatures. While raising the temperature to a particular value care was taken to avoid rapid heating.

Heat treated samples, after cooling, were tested on a Universal Testing Machine for tensile splitting strength. In this test cylindrical specimen is placed on its curved surface between the platens of the testing machine and the load is applied until the failure occurs by splitting along the vertical diameter. Tensile

splitting strength⁵⁸ is then calculated by using the relation

$$T = \frac{2\bar{P}}{\pi LD}$$

where \bar{P} is the compressive load at which fracture occurs, L is the length of the cylinder and D its diameter. From the calculated tensile splitting strength values, compressive strength can be estimated approximately following the conversion factor

$$\text{Compressive Strength} = 10 \times T .$$

Apart from strength determination, high temperature measurements involving the determination of expansion/shrinkage during the first heating and cooling cycle of the refractory concrete were also done. For this purpose cylindrical pellet was made as described above. The apparatus comprised quartz tube of 1.5 cm. diameter and 18 cm. length in which a small bead of quartz was kept at the bottom. Pellet to be examined was placed on top of this bead and a quartz rod of 1 cm. diameter and 18 cm. length was rested on top of the pellet. A dilatometer was attached to the top end of the quartz rod in order to measure the contraction or expansion, as the case may be. The pellet was heated by placing the assembly inside a

vertical column furnace. Length of the furnace column was such that only half of the tube was inside the furnace. The temperature of the pellet was recorded by a thermocouple junction placed near the pellet and the leads were taken out and connected to a potentiometer.

Before starting the actual experiment, a run was made without the pellet so as to note the small amount of expansion/contraction in quartz, and this was accounted for in the actual readings.

3.2 Results and Discussion

3.2.1 Portland Blastfurnace Slag Cement:

Using ground granulated blastfurnace slag and ordinary Portland cement following three compositions were made:

Composition I	95 per cent Portland cement and 5 per cent slag	by weight
Composition II	90 per cent Portland cement and 10 per cent slag	
Composition III	80 per cent Portland cement and 20 per cent slag	

Compressive strength values as a function of curing age for these compositions are tabulated in Appendix 1 and graphically shown in Fig. 2.

It is observed that at all ages (up to 4 weeks) strength decreases with increasing slag content in the mix. In composition I strength continues to increase up to 21 days and thereafter rate of increase of strength decreases and curve tends to become flat. In other two compositions strength builds up to 3 weeks almost in a similar manner as in composition I but after three weeks, instead of becoming flat, strength increases at relatively faster rate. This observation is attributable to the hydration of slag, which hydrating slowly makes its contribution to the strength at later ages only.

For comparison purpose Fig. 2 also includes the strength vs. age behaviour of Portland cement mortars. It will be noticed that for composition II and composition III though the compressive strength is less at early ages, it exceeds pure Portland cement values at higher ages. This also strengthens the view that slag hydration is contributing to strength at higher ages.

Composition I which contains relatively less slag (5 per cent by weight) shows a strength development behaviour which is similar to that of Portland cement. But the strength of composition I cement at all ages is more than Portland cement strengths. Possible reason for this unexpected observation can either be better particle

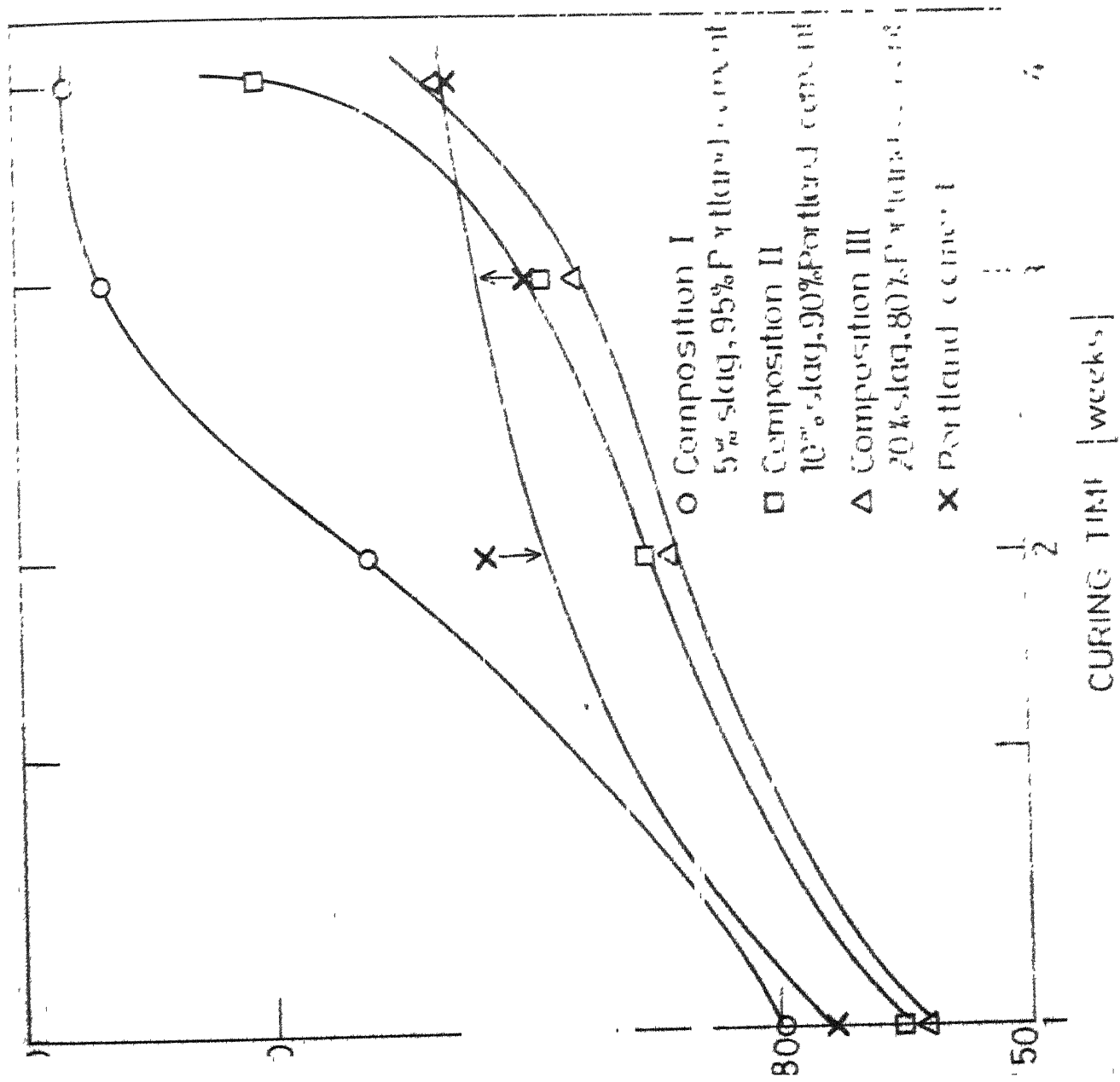


Fig. 2

packing or some change or variation in casting and curing conditions for either the composition I or the Portland cement.

The same data is depicted in a different manner in Fig. 3 where the compressive strengths are shown as a function of the slag additions at ages 1, 2, 3 and 4 weeks. Initially with the additions of slag (up to 10 per cent) strength decreases rapidly at all ages but beyond 10 per cent addition, the rate of decrease in the strength becomes less.

Regarding the setting time (Table 3.2) determination of these cements it was observed that initial setting time is not much changed by slag addition but the final setting time increases with increase in the slag in the mixture.

Table 3.2
Initial and final setting times of Portland
blastfurnace slag cements

Composition	Initial setting time (minutes)	Final setting time (minutes)
Composition I (95 per cent Portland cement, 5 per cent slag)	28	72
Composition II (90 per cent Portland cement, 10 per cent slag)	37	148
Composition III (80 per cent Portland cement, 20 per cent slag)	35	156

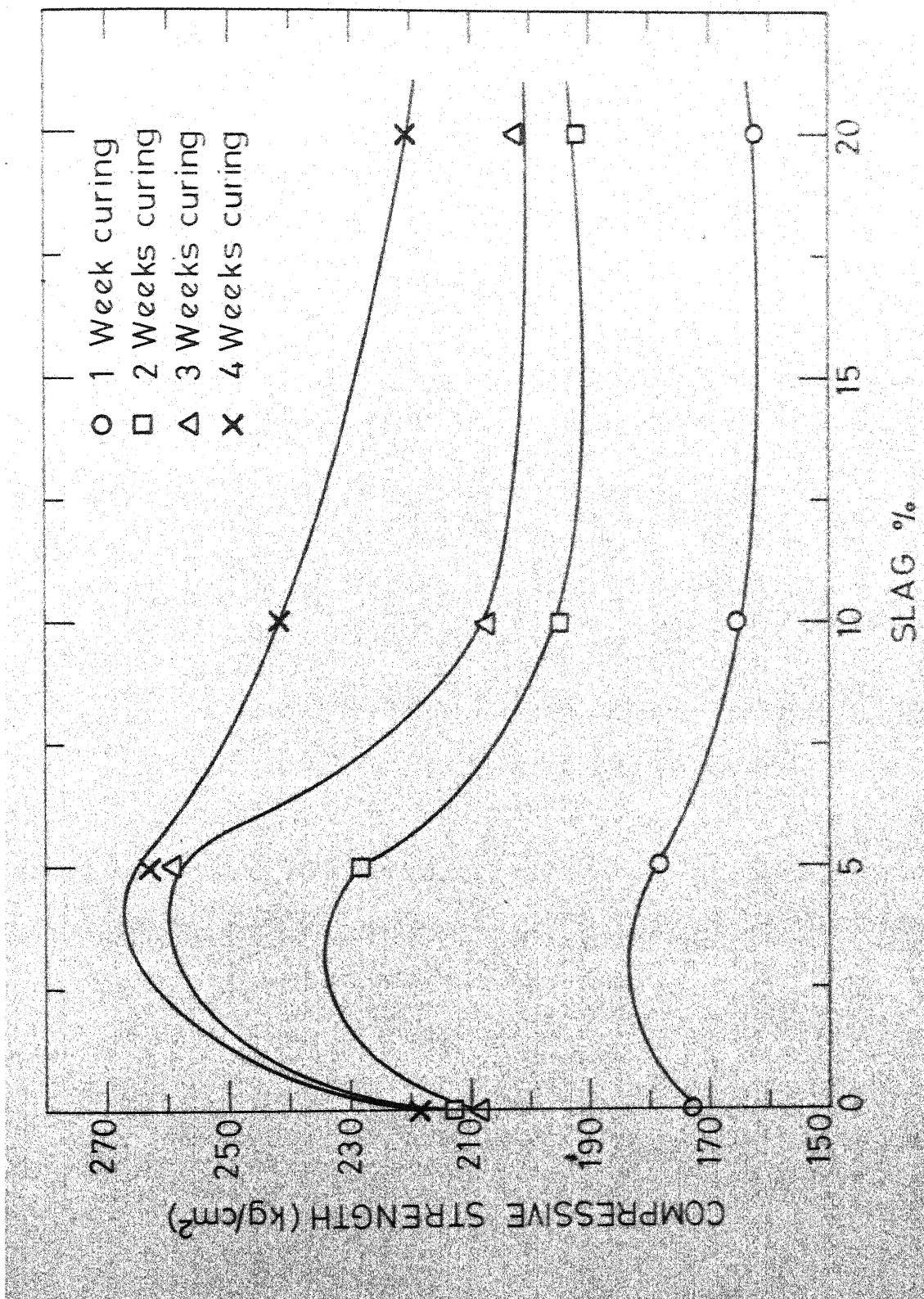


Fig. 3

During the tests it was observed that surface abrasion resistance of the cured mortars for all the three compositions was almost the same, but the workability (at the same consistency) was slightly improved with slag addition.

3.2.2 Supersulfated Cement:

Two compositions of supersulfated cement given below (called composition IV and V hereafter) were prepared.

Composition IV	85 per cent slag, 10 per cent plaster of Paris and 5 per cent Portland cement	by weight
Composition V	80 per cent slag, 15 per cent plaster of Paris and 5 per cent Portland cement	

In these compositions plaster of Paris ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) was used instead of dead burnt gypsum employed in earlier reported work. Idea behind selecting the composition with relatively low activator, only 10 and 15 per cent as against 20-25 per cent recommended by Chopra and Lal⁴⁹ for Indian slags characterized by higher alumina content, was to see whether reasonably good strength can be obtained by a lower degree of activation. Reduction in the amount of the activator will be an important step towards reduction of the cost of the cement.

Compressive strength values for 1:3 mortars cube as a function of curing age for both the compositions have been tabulated in Appendix 2 and plotted in Fig. 4. For comparison the compressive strengths for Portland cement are also shown in the same figure.

For both the compositions one week strength is appreciably less than that obtained with Portland cement. In the case of composition IV, strength remains below the Portland cement strength for about six weeks and after that it rises continuously and exceeds. On the other hand, the strengths of cubes made of Portland cement and composition V become equal after two weeks only and thereafter, whereas the former rises slowly, the strength of composition V increases rapidly. After about four weeks the levelling off in strength suggests that the calcium sulfate has almost fully reacted with alumina etc. to give strength developing hydrated compounds.

Composition V develops strength at a faster rate as compared to composition IV. This rate and the progressively accelerating action, for first few weeks, of calcium sulfate depends, according to Blondiau⁸ on the one hand, on the quantity of the activator present, which is regulated so that the whole of the alumina can combine itself into sulfoaluminate, and, on the other hand, on its solubility

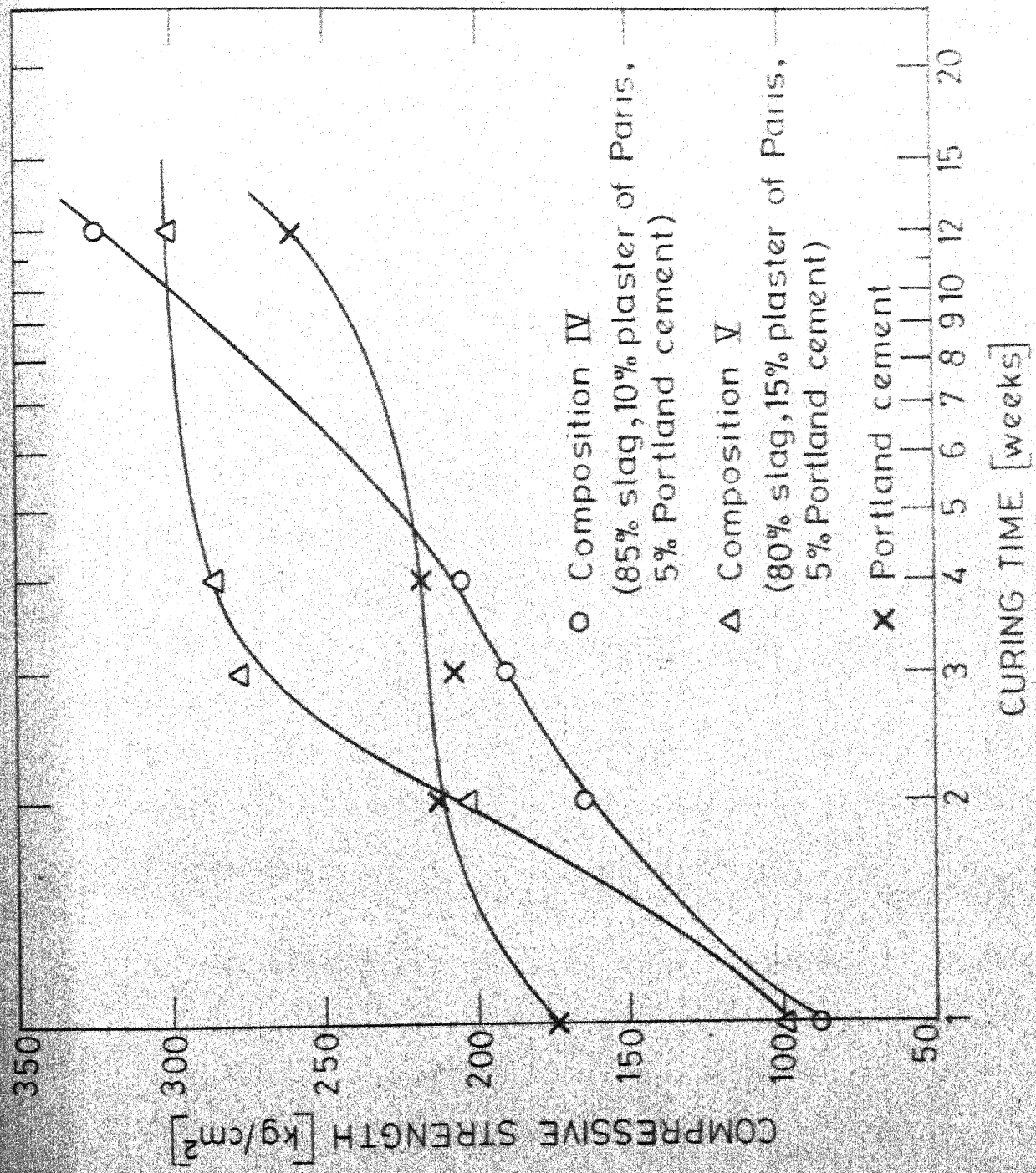


Fig. 4

which must be maintained at an adequate level in order to permit the calcium sulfate solution in proportion to the content of lime and soluble alumina.

Final strengths, after 12 weeks, for compositions IV and V are quite close. Although the trend of the curve for composition IV seemingly indicate a further increase after three month, yet on the basis of the flattening of the curve for composition V as well as the observations of Chopra and Lal we expect that strength for composition IV will tend to become almost constant beyond 12 weeks.

Since the early strength of composition IV is less as compared to that of composition V, the latter was taken up for further studies as it will make a suitable super-sulfated cement for mass concreting works. Even for composition V, it should be noted that care will have to be taken while using the cement in cold climates where the early strength will be adversely affected because of substantially slower rate of hydration.

Concrete cubes (15 x 15 x 15 cu.cm.) from composition V were made using a water/cement ratio of 0.5. But the cubes obtained had honeycomb structure and hence when tested for compressive strength gave very low values (Table 3.3). However, one cube which did not have honeycombs and was kept for 4 weeks curing, gave strength

Table 3.3

Compressive strength values of 1:2:4 concrete cubes of supersulfated composition V (80 per cent slag, 15 per cent plaster of Paris, 5 per cent Portland cement)

Water/cement ratio	Compressive strength (Kg/cm ²)				
	1 weeks	2 weeks	3 weeks	4 weeks	12 weeks
0.5	19.0	13.2	160.0	71.2	
	17.0	52.2	122.2	53.0	251.0
	16.0	214.4	136.2	326.0	
Average	17.3	93.3	139.4	150.1	251.0
0.75	46.6	112.2	133.3	104.4	
	44.0	66.6	160.0	171.1	200.0
	38.2	75.5	128.4	125.5	
Average	42.9	84.7	140.5	133.6	200.0

value as high as 326 Kg/cm² which means that good strength can be obtained if the cubes are properly cast. Therefore, the test was repeated with water/cement ratio of 0.75 which was determined by the slump test. Again as shown in Table 3.3 strength values were not at all satisfactory. In fact during casting it was observed that this water amount though determined by the slump test was in fact more than needed but it gave correct slump because of the quick setting action of the cement (see setting time below). This was also the reason for the appearance of honeycomb structure

when low water/cement ratio (0.5) was used. Conclusive tests on concrete could not be done as the test consumed large amounts of material and not enough slag was available. However, on the basis of above results, a water/cement ratio of somewhere between 0.5 and 0.75 should result in cubes without honeycombs and hence should give good strength values.

As hydrated lime is also used in place of Portland cement in supersulfated mixes, another mixture called composition VI hereafter, containing 80 per cent slag, 15 per cent plaster of Paris and 5 per cent hydrated lime, was prepared. The compressive strengths of mortars cubes are listed in Appendix 3. The same results plotted in Fig. 5 show quite low strength as compared to the strength obtained in the case of compositions IV and V at all ages. The lesser strength values of lime activated supersulfated cement, as Lea³ has suggested may be due to a saturated lime solution which results in low strengths. This indicates that hydrated lime in smaller proportions might give improved results. However, use of lime activator may lead to deterioration of cement in storage due to carbonation of lime. Hence, in view of these facts it is preferable to use Portland cement instead of hydrated lime.

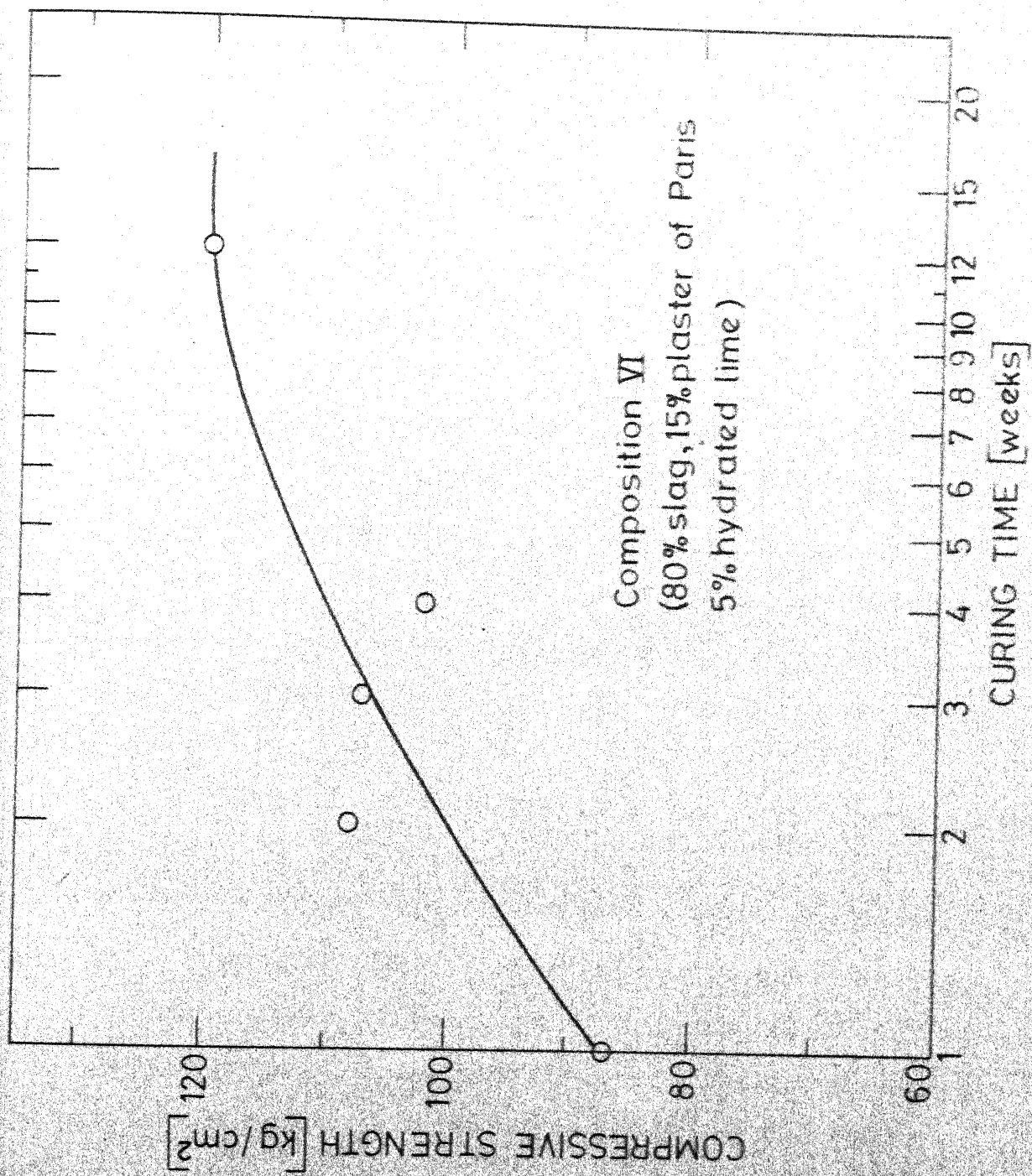


Fig. 5

3.2.3 Setting Times:

Initial and final setting times of composition V were also determined and the values obtained are given below:

Initial setting time = 6 minutes

Final setting time = 75 minutes.

Since the initial setting time is quite short, the paste was remixed in order to make sure that this quick setting is not caused by 'False Set' of the cement paste.

Quick setting of the supersulfated cement may be partially due to the higher amount of alumina present in the slag but a more convincing reason is the presence of plaster of Paris which renders the cement quick setting when present in large quantities. In addition, the setting action of plaster itself leads to a stiffening of cement paste.

Because of quick setting action, the cement is not workable, and unless and until its setting time is brought to the practical limits by using retarders, it cannot be put to any use. Since keratin, a protein which acts as a retarder for plaster of Paris³ was not available conventional retarders used in cement industry were tried. Various retarders and their effect on setting time are listed in Table 3.4.

Table 3.4

Effect of additives on initial setting time of composition V
(80 per cent slag, 15 per cent plaster of Paris, 5 per cent
Portland cement)

Additive	Amount wt %	Initial setting time (minutes)
Calcium chloride	1.0	7
	2.0	7
Sodium carbonate	1.0	7
Sodium oxalate	1.0	6
Sugar	2.0	14
Boric acid	0.2	80
	0.1	44
Borax	0.1	11
	0.15	20
	0.175	31
	0.20	60
	0.25	> 60
	1.00	> 60
	3.0	> 60

Additives like calcium chloride, sodium carbonate, sodium oxalate did not have any influence on the setting time. Only sugar, boric acid and borax additions helped in increasing the setting time. Of these three, use of sugar will not be economically viable, for as the results show, a larger percentage of this will be needed to bring the setting time to a practical range.

Both boric acid and borax are equally effective and their small amounts are sufficient to increase the setting time considerably. However, as the commercially available borax is cheaper as compared to boric acid, it is preferable to use the former. Figure 6 presents the effect of the amount of borax addition on the setting time. As indicated, only 0.2 per cent addition of borax is enough to raise the initial setting time from 6 minutes to a workable range of 50-60 minutes. Final setting time with this addition was found to be 110 minutes.

In order to see if the addition of borax has any effect on the strength compressive strength tests on mortar cubes made out of borax retarded composition V (called composition V-Bo hereafter) were carried out. The results are listed in Appendix 4 and shown in Fig. 7. Amount of borax was just 0.2 per cent as found above. As expected borax retards the hydration at early ages and thus the strength of the retarded cement is less as compared to that of unretarded. However, after 4 weeks it catches up with the unretarded cement and after 12 weeks even becomes slightly more.

Since other investigators who have studied super-sulfated cement using dead burnt gypsum as the activator did not report any problem with setting time, a mixture

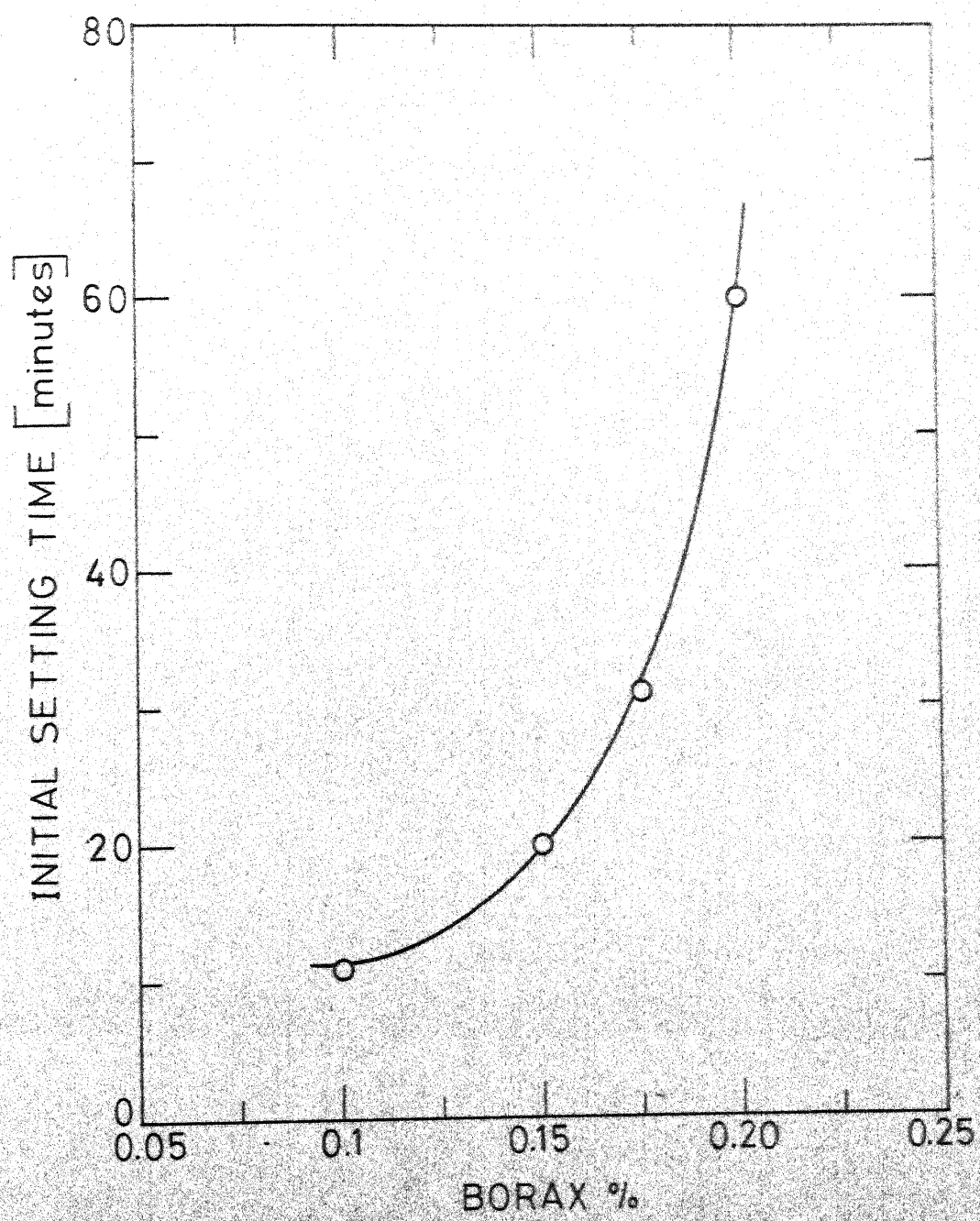


Fig. 6

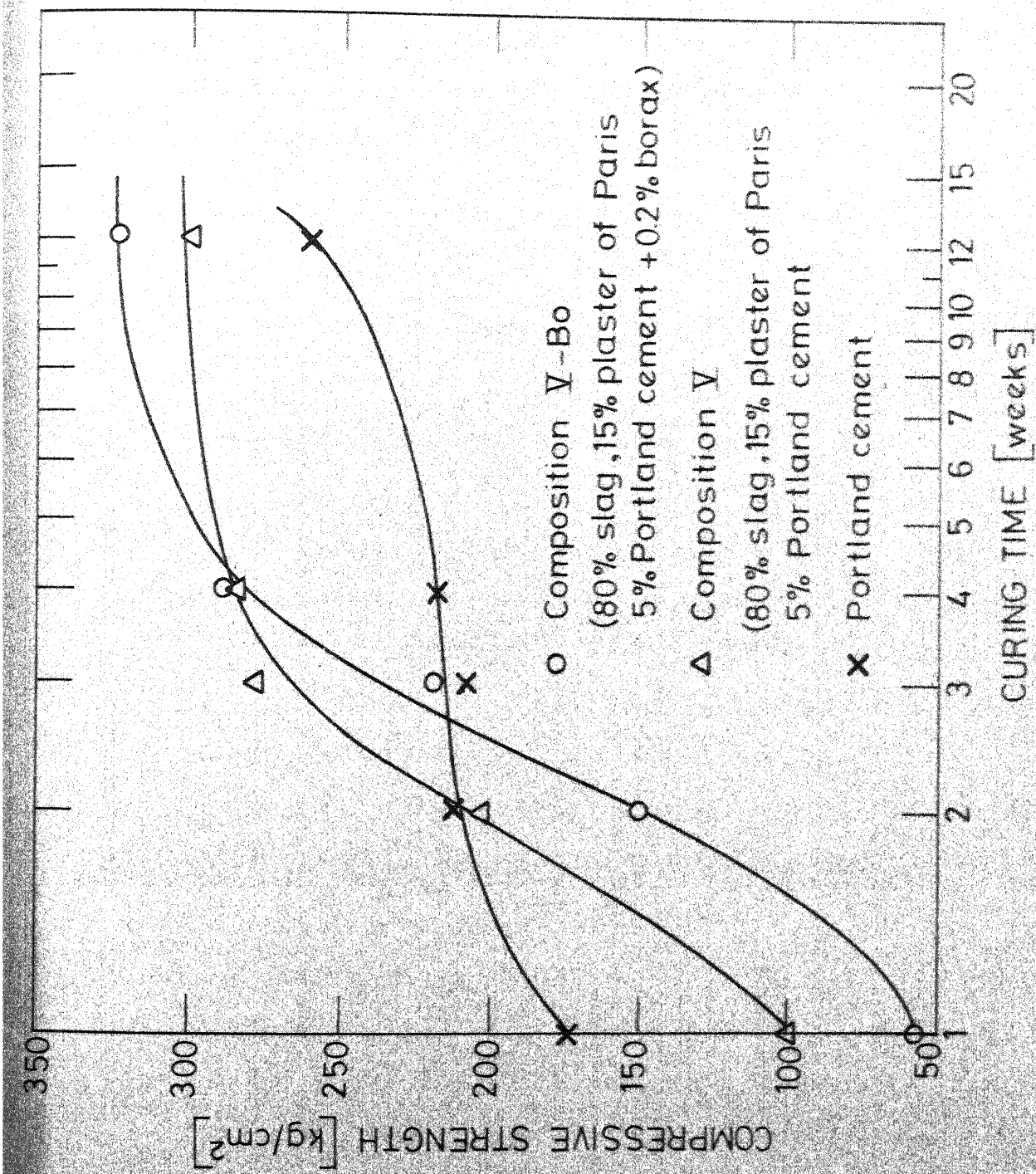


Fig. 7

called composition VII, in which whole of the plaster of Paris in composition V was replaced by the same weight of gypsum burnt at 750°C for 8 hours, was prepared and its initial and final setting time values were determined:

Initial setting time = 5 hours

Final setting time = 9 hours 30 minutes

The compressive strength values of mortar cubes of this cement (Appendix 5) are plotted in Fig. 8. Early strength (one week) of this cement is close to that obtained in the case of compositions IV and V but at higher ages it fails to rise as rapidly as it does for compositions IV and V and, hence falls quite short of the values attained by these compositions. Although the compressive strength of composition VII is less as compared to those of compositions IV and V, yet it gives, qualitatively speaking, better surface finish, and surface abrasion resistance.

Since composition V had a short initial setting time whereas composition VII had a very long initial and final setting times, attempt was made to control the setting time of composition V by using a mixture of plaster of Paris and hard burnt gypsum. These mixtures which were tried had hard burnt gypsum to plaster of Paris weight ratio of 1:3; 1:1 and 3:1. The setting times for these mixtures used as activators, are shown in Table 3.5.

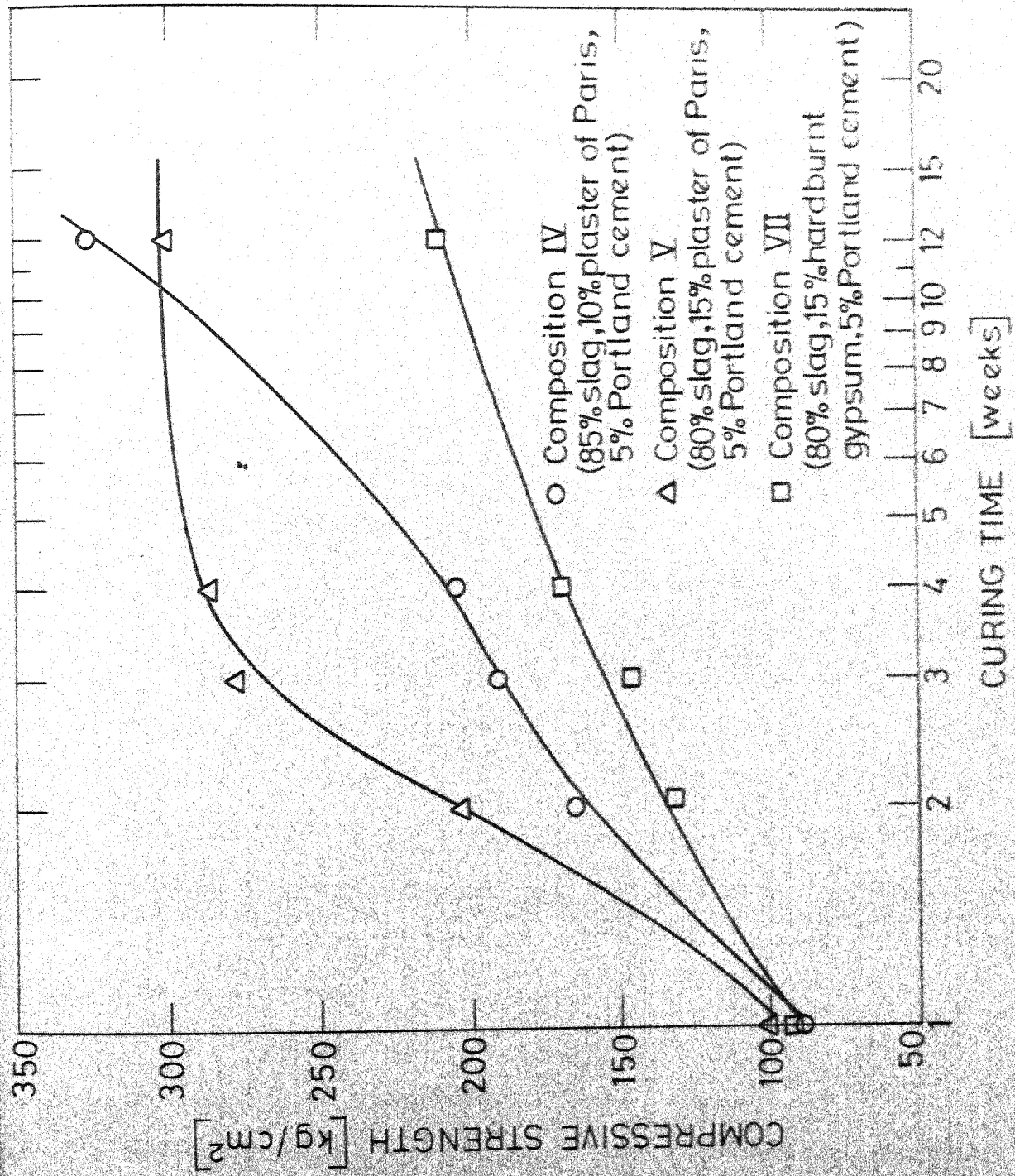


Fig. 8

Table 3.5

Initial setting times of hard burnt gypsum and plaster of Paris mixture activated composition V (80 per cent slag, 15 per cent hard burnt gypsum + plaster of Paris mixture, 5 per cent Portland cement)

Hard burnt gypsum : Plaster of Paris (by weight)	Initial setting time (minutes)
1:3	6
1:1	8
3:1	10

The mixture containing hard burnt gypsum and plaster of Paris in the ratio of 1:3 had the initial setting time of 6 minutes which is the same as obtained when pure plaster of Paris was used. In other mixture of ratio 3:1 the setting time increased by 4 minutes to 10 minutes. This suggests that even one part of plaster of Paris with three parts of hard burnt gypsum is enough to cause the quick setting of the cement paste.

As the gypsum and plaster of Paris mix did not work as far as the control of the setting time is concerned, borax was the only suitable retarder and thus composition V retarded by 0.2 per cent of borax was considered a workable mixture for making supersulfated cement.

3.2.4 Supersulfated Cement Made from Kalinga Slag:

Since the Hindustan Steels Limited showed a great interest in the problem of utilization of blastfurnace slag in making cements a slag obtained from Kalinga (HSL, R & D) was also tried for making supersulfated cement. Chemical analysis of this slag is given in Appendix 6. Compressive strength values for mortars of composition V using Kalinga slag are plotted in Fig. 9 (Appendix 7). Early strength is low, but final strength though lesser than that obtained by TISCO slag, is reasonably good. Lesser strength obtained with this slag as compared to that obtained with TISCO slag can be attributed to the presence of crystalline phases and a less reactive structure of glassy phases in the former slag.

3.2.5 Interpretation of X-ray and DTA Analysis:

Figure 10 shows the X-ray diffraction patterns, numbered 1 to 5, of Kalinga slag, TISCO slag, unhydrated, 1 week hydrated and 4 weeks hydrated supersulfated cement composition V, respectively. In both the slags, because of their glassy nature only a few peaks are observed. Both the slags show two broad humps in the 2θ angle range between 18° and 25° . These humps which are more marked

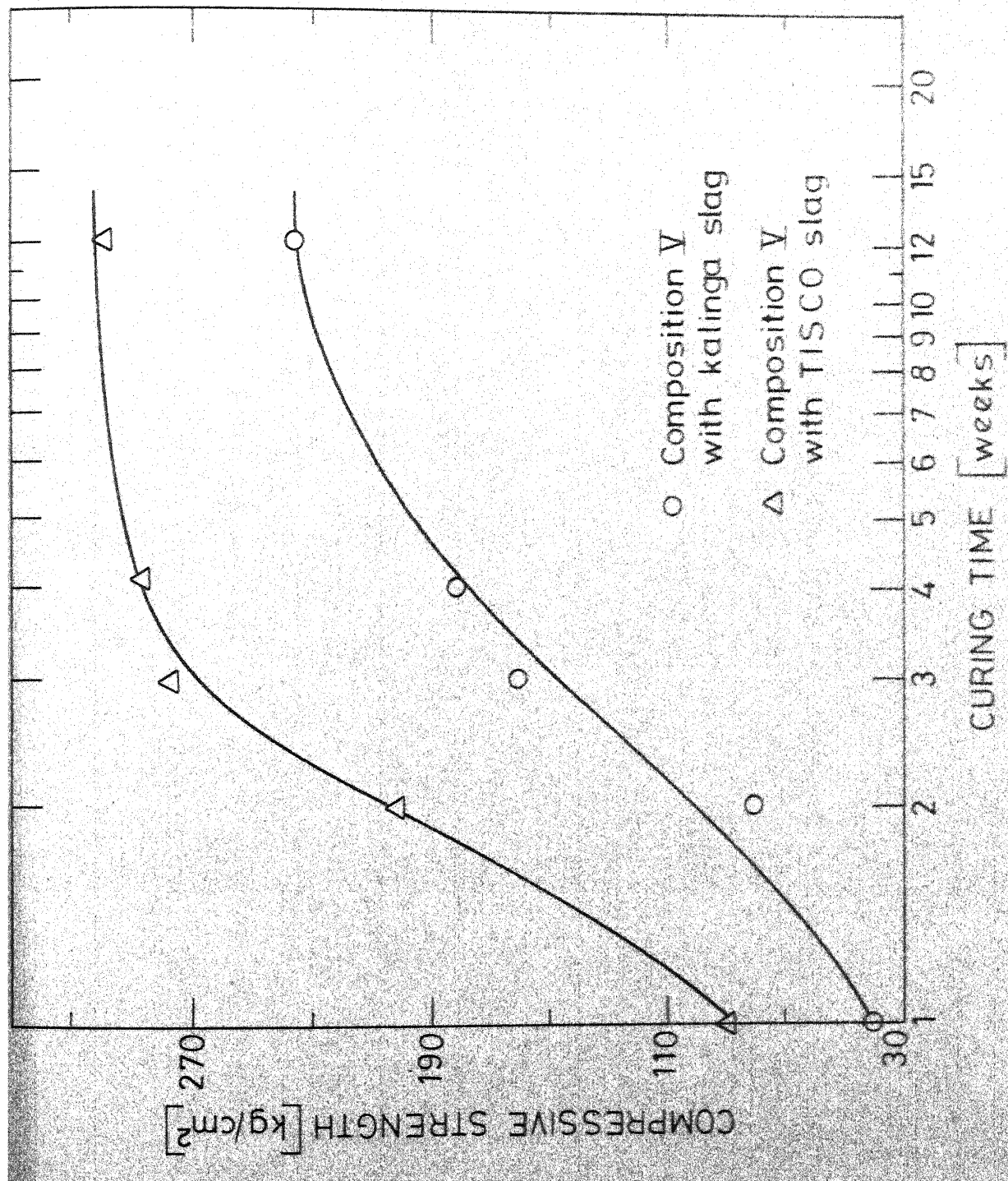


Fig. 9

in TISCO slag, are probably due to melilite series of solid solutions. Gehlenite is also observed in the slags at 3.068 and 2.851 Å. But since there are no other peaks to confirm the identification of this compound this conclusion may be questionable. The Kalinga slag gives one peak at 3.336 Å, which corresponds to the presence of free silica in the slag. In the case of TISCO slag a sharp peak at 2.44 Å, as well as a wide peak at 2.019 Å, is observed. These peaks are probably spinel peaks.

In unhydrated composition V diffraction pattern broad humps in the angle range between 18 and 25° are retained as they are in slag pattern and in addition to slag peaks there occur plaster of Paris peaks (ASTM X-ray Powder Data Card No. 14-453) at 6.02, 3.476, 3.00, 2.80, 1.843, 1.690 and 1.66 Å. A small peak at 3.338 Å is due to small amount of silica, present as an impurity in plaster of Paris.

Curves number 3 and 4 showing 1 week and 4 weeks hydrated cements throw light on a few of the important facts. If intensities of plaster of Paris peaks in curve number 3, 4 and 5 are compared, it can be concluded that plaster of Paris is being used up during hydration process. It is noted that after 4 weeks hydration plaster of Paris peaks almost vanish meaning thereby that almost all the plaster of Paris has been consumed in the reaction. Plaster

of Paris peak at 3.00 \AA which does not vanish develops a definite change in shape as the hydration progresses. This suggests the formation of some hydration product which gives rise to a peak near 3.00 \AA . This hydration product is probably tobermorite type⁵⁹ whose other peaks appear at about 2.786 and 1.82 \AA . Since the peaks corresponding to tobermorite are not very sharp it is quite probable that the compound is in the gel or poorly crystallized form.

Tobermorite peak at 2.786 \AA overlaps the plaster of Paris peak at 2.80 \AA and that is why after 4 weeks hydration when plaster of Paris is consumed, tobermorite peak's intensity though actually increasing appears to be decreasing.

Another very distinct observation is the enhancement of intensities of the two humps in the 2θ angle range between 18 and 25° . This is probably due to the formation of various calcium silicate, aluminate hydrates which give rise to peaks in this region. Hump around 20° shows another feature by splitting into two peaks one at 4.413 and another at 4.271 \AA . The intensity of the latter peak increases with hydration. This peak probably corresponds to a compound of the type $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ (ASTM X-ray Powder Data Card No. 3-594) whose other peaks occur around 3.04 , 2.688 , 1.91 , 2.45 and 2.86 \AA . Hydration products in the humped

region seem to have important bearing on the final strength of the cement.

The presence of calcium aluminate hydrate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8-12\text{H}_2\text{O}$ (ASTM X-ray Powder Data Card No. 2-83) is observed around 7.62, 3.81, 2.86, 2.45 and 2.29 Å. Since peaks for calcium silicate hydrate, $5\text{CaO} \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ (ASTM X-ray Powder Data Card No. 12-475) also lie almost close to above mentioned d values therefore the possibility of this compound also cannot be ruled out.

Ettringite (ASTM X-ray Powder Data Card No. 9-414), which is high sulfate form of calcium sulfoaluminate hydrate, appears only after 4 weeks and gives rise to peaks at 9.75, 5.61, 2.56, 2.20 and 2.154 Å. This observation means that strength development during first few weeks is only due to tobermorite, and calcium aluminate hydrates and it is only after a few weeks that ettringite makes its contribution.

The possibility of a low sulfate form of sulfoaluminate hydrate also exists but since the peaks for this compound mainly lie in the humped region nothing definite can be concluded.

It is to be noted that there are no peaks corresponding to $\text{Ca}(\text{OH})_2$ and this observation supports the view that no or very little $\text{Ca}(\text{OH})_2$ is produced in the hydration of these cements.

Figure 11 shows the diffraction patterns of hydrated forms of composition V-Bo and composition VII. In the case of composition V-Bo the hydration products are exactly the same as obtained for composition V but one major difference lies in the rate of hydration. Here, after one week hydration intensity of humps does not increase much indicating that the hydration is taking place at a slower rate. Thus results of the X-ray analysis are in good agreement with the observations on compressive strength tests on 1:3 mortars which indicated that the borax addition retards the strength development process. As indicated in the diffraction pattern, hydration rate increases after one week and during next few weeks enhancement of hump intensities takes place and peaks corresponding to tobermorite, calcium silicates calcium aluminate hydrates and ettringite appear.

Pattern 5 in this figure corresponds to one week hydration of composition VII where instead of plaster of Paris hard burnt gypsum was used. Here, in contrast to compositions V and V-Bo, ettringite is formed after one week only but the humps in the 2θ angle range between 18° and 25° remain almost unchanged. Hump at 20° is slightly modified in the sense that it spreads more towards the lower angle side indicating the formation of some amorphous

phase. Sharp peaks at 3.49, 3.02, 2.84, 2.324 and 2.204 Å correspond to unreacted hard burnt gypsum (ASTM X-ray Powder Data Card No. 6-226). By comparing the heights of the peaks of plaster of Paris in Fig. 10 and that of hard burnt gypsum in Fig. 11 after one week hydration it can be readily concluded that with plaster of Paris the hydration process is faster. This can be possibly explained by the fact that presence of CaSO_4 in solution, according to Bloindau, affects the rate of reaction, and since the plaster of Paris is more soluble (0.3 gm in 100 gm) as compared to hard burnt gypsum (0.2 gm in 100 gm) the composition using plaster of Paris hydrates faster. Fast action of plaster of Paris is also supported by the data obtained for the compressive strength values for the two compositions viz. V and VII.

Regarding the formation of ettringite after one week only in composition VII, it can only be said that D'Ans and Eick⁵⁶ have mentioned that conditions of alkalinity and rate of supply of SO_4^{--} ions (which depend upon the temperature of burning of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to make CaSO_4) affect the formation of ettringite and other related phases at early ages. Thus in view of these facts it can be favourably concluded that early formation of ettringite in the case of composition VII is not due to faster rate of hydration.

In the end of this discussion, again coming back to Kalinga slag a comment can be made regarding the lesser strength of composition V using this slag as compared to that using TISCO slag. One reason for this is probably the presence of free silica as indicated by X-ray diffraction, in the Kalinga slag that renders the slag less active. Another possible reason as already mentioned before is perhaps the difference in the glass structure of two slags.

Results of DTA analysis done on unhydrated composition V and hydrated forms of various compositions are shown in Fig. 12. For comparison sake DTA of TISCO slag, which gives an endothermic peak at 810°C and a characteristic exothermic peak at 930°C due to devitrification of slag is also included in the same figure. DTA curve of unhydrated composition V, in addition to slag peaks, gives one more endothermic peak at 165°C due to dehydration of plaster of Paris. One week hydrated compositions V and V-B₀ show another small endothermic peaks at 140°C which can be attributed to dehydration of calcium silicate hydrates. After 4 weeks hydration these peaks show an increase in the intensity. Since silicate hydrates aluminate hydrates, ettringite and tobermorite^{60,61} all give endothermic peaks in the temperature range between 120-200°C identification of each of these individually in

this temperature range becomes difficult. However a broad peak such as the one observed here in this temperature range surely suggests the possibility of the presence of these compounds. The endothermic peaks seen at 185°C can either be due to low sulfate form of sulforaluminate hydrate or calcium aluminate hydrates. Sharp exothermic peaks at 910°, observed in all the hydrated samples are characteristics of tobermorite⁶². It is noted that the intensity of these increase with hydration whereas as another exothermic peak at 930°C, which is due to slag devitrification, disappears after 4 weeks hydration. In hydrated samples endothermic peaks at 820°C which overlaps with 810°C endothermic peak of slag can be possibly ascribed to calcium silicate hydrates⁵⁷. One week hydrated composition VII exhibits an endothermic peak at 130°C due to ettringite. Another endotherm observed at 410°C is not explained.

3.2.6 High Temperature Properties of Supersulfated Cement Concrete:

Expansion/shrinkage test was carried out on a pellet of 1.27 cm. in diameter and 3.34 cm in height. Results of this test are presented in Appendix 8 and plotted in Fig. 13. As indicated in the figure, the specimen shows a near reversible expansion/shrinkage

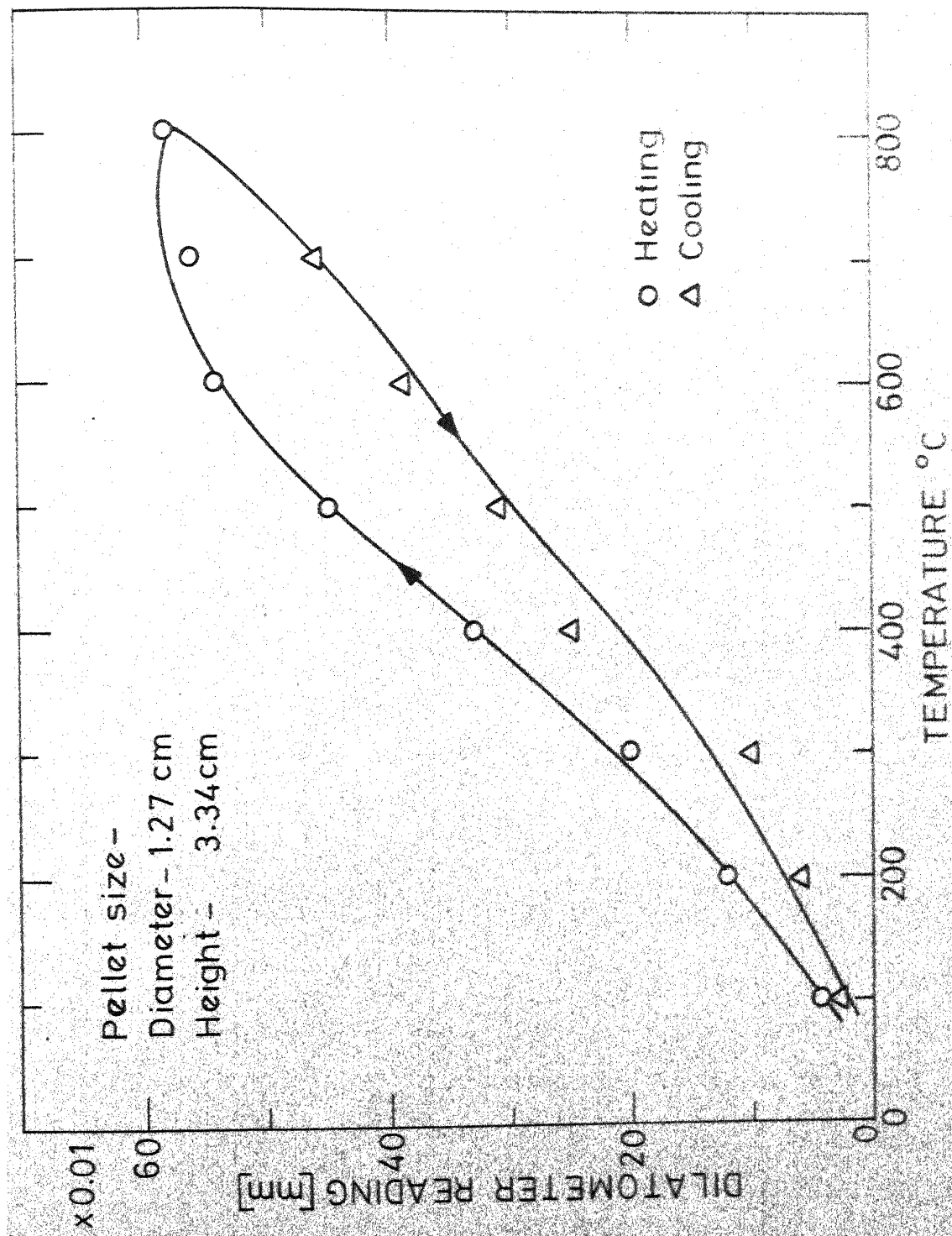


Fig.13

behaviour with heating/cooling. As discussed in Chapter 2 the overall expansion with temperature during the first heating cycle can be due to superposition of larger expansion of fire brick grog over the lesser shrinkage of the cement. The total expansion observed up to 800°C is just 0.58 mm. i.e. 1.7 per cent which is not significant to cause any appreciable influence on strength of the structure.

The results of tensile splitting strength tests on the cylindrical pellets as a function of temperature are listed in Appendix 9 and plotted (in terms of compressive strength) in Fig. 14. To have a comparative idea values for pellets made from high alumina cement, which is the standard hydraulic refractory cement, have also been included.

At all temperatures, below 900°C the strength of slag cement pellets is very low in comparison with alumina cement pellets. Reason for it lies in the fact that before being subjected to high temperatures, the pellets were water cured for one week during which alumina cement pellets being rapid hardening developed almost all of their strength whereas the supersulfated cement pellets hydrating slowly attained only a part of the strength.

As expected, in both the cements strength values decreased with increasing temperature up to a limit and then again showed an increase. Thus there existed a

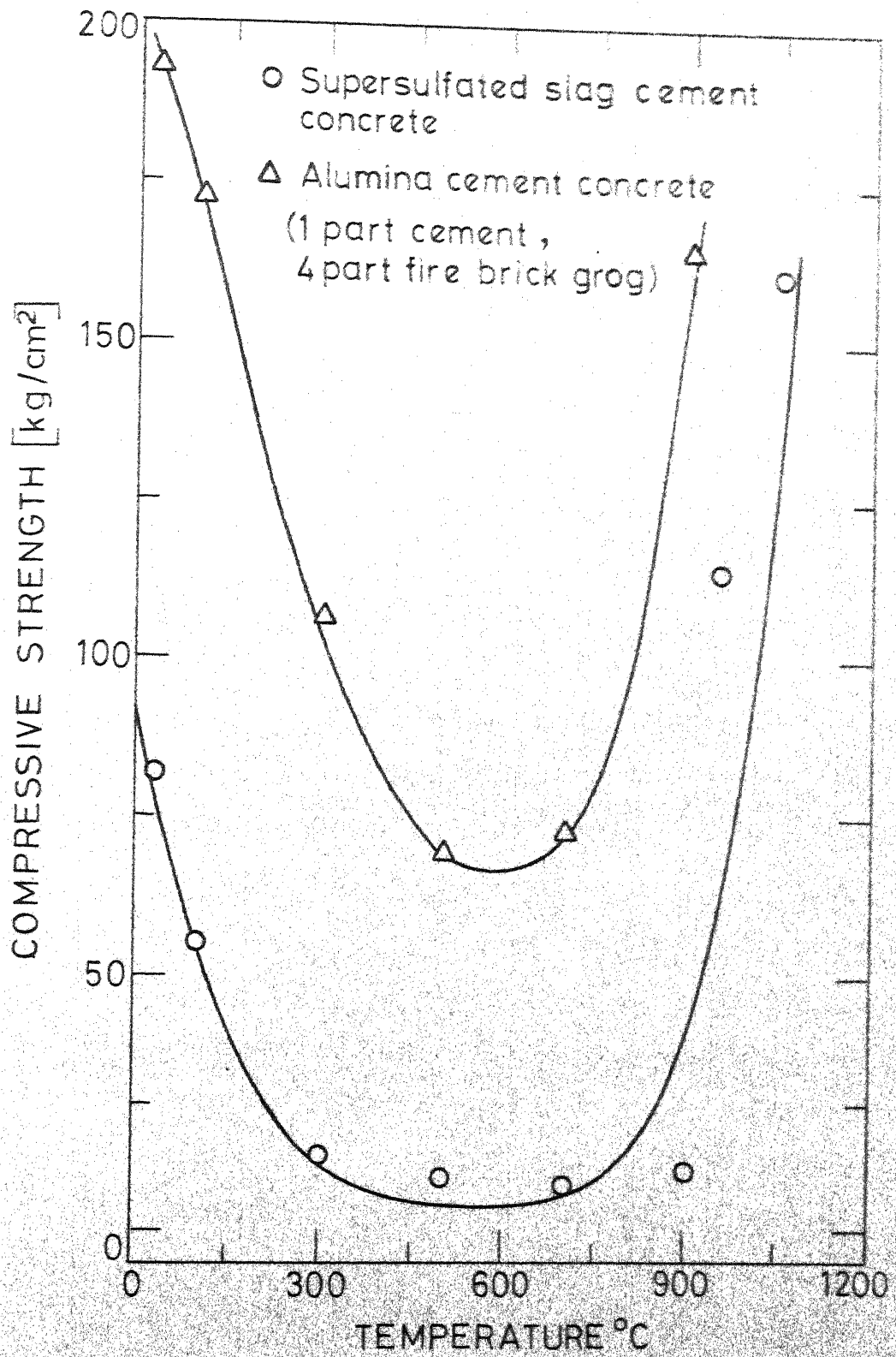


Fig-14

- (6) Because of the presence of plaster of Paris, supersulfated cement composition V has a very short initial setting time. But this short time can be lengthened to workable range by the addition of 0.2 per cent borax. Composition V without the addition of borax or any other retarder can be used in making precast slabs etc. for structural purposes because it can be demoulded quickly.
- (7) Borax addition retards the strength development process in the beginning but at later stages, the strength of borax retarded cement catches up with that obtained without borax.
- (8) Use of hydrated lime in place of Portland cement in composition V is not preferable for it gives lower strength.
- (9) Comparison of the results of the tests carried out on compositions V and VII clearly indicate that it is preferable to use plaster of Paris to hard burnt gypsum in making supersulfated cements. This is a very important observation because considerable improvement in strength can be obtained by keeping the composition and everything else the same but using plaster of Paris in place of the hard burnt gypsum. Use of plaster of Paris might have a

favourable bearing on the economics of the cement making process also because hard burnt gypsum is obtained by firing the natural gypsum at around 700°C whereas for plaster of Paris, temperature in the range of 120 to 130°C is needed.

- (10) In view of the fact that the initial strength is low, all the cements utilizing slag as one of the ingredients should be carefully used in cold climate because of slower rate of hydration at low temperatures.
- (11) TISCO slag makes better cement as compared to Kalinga slag.
- (12) X-ray analysis results show good agreement with the compressive strength tests on 1:3 mortar cubes. Various calcium silicates, calcium aluminate hydrates, tobermorite and ettringite phases are observed as the hydration products of compositions V and V-Bo. Composition VII shows the presence of ettringite after one week. No other hydrated crystalline phase could be observed. However, possibility of some amorphous phase is indicated.
- (13) High temperature properties of supersulfated cement, as far as strength is concerned, does not match with alumina cement properties. However, supersulfated cement shows a permissible expansion/shrinkage on

heating/cooling. Stability of this cement towards lime hydration is better than Portland cement.

Since the problem of utilization of blastfurnace slag is of gross importance, thorough research work should be done in the various aspects of the problem. As far as the Portland blastfurnace slag cements are concerned Associated Cement Companies make this cement with about 40 per cent additions of slag. Still higher additions of slag up to 60 per cent should be tried. With a good quality slags even this much addition should result in a reasonably good cement which can be successfully used in tropical regions.

Regarding supersulfated cement more work is needed to be done in finding out a composition which will give best results when $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ with Portland cement is used as an activator. Here a more careful study of the effect of amount of plaster of Paris and Portland cement should be made.

Since in this study strength tests on concrete blocks could not be carried out successfully, therefore this aspect of the problem should also be investigated.

In controlling the setting time of supersulfated cements, retarders other than borax should be found. Investigations should be carried out using keratin and

P_2O_5 , which retard the setting of plaster of Paris. These two probably will not have any adverse effect on the hydration rate of the cement and hence may become more suitable retarders than borax.

Since the supersulfated cements are white in colour they can be easily used in making coloured cements and hence a study should be made on the effect of colouring agents on the strength of the cement.

In making supersulfated cement a major portion of the cost involved is in grinding of the slag therefore the effect of grinding on strength should also be investigated and an attempt should be made to improve the granulation process so that slags with better grindability result.

As the tests with supersulfated cements in making cold bonded iron ore pellets could not be completed it is recommended that a research should be conducted to explore this possibility of using supersulfated cement in this field because it will be of immense importance to the steel industry.

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APPENDIX 1

Compressive strength values of 1:3 mortar cubes of Portland and Portland blastfurnace slag cements.

Composition	Compressive strength (kg/cm ²)				
	1 week	2 weeks	3 weeks	4 weeks	2 years
Composition I (95% Portland cement, 5% slag)	179.0 178.0 178.5	218.5 222.0 245.0	254.5 265.0 250.0	263.0 263.5 183.0	-
Average	178.5	228.5	259.5	263.2	-
Composition II (90% Portland cement, 10% slag)	159.0 177.0 160.0	188.0 197.5 193.5	200.0 208.5 212.5	240.5 244.0 238.5	-
Average	165.3	195.0	207.0	241.0	-
Composition III (30% Portland cement, 20% slag)	171.0 151.0 165.0	193.0 191.0 192.0	215.0 191.0 -	244.0 215.0 231.9	-
Average	162.3	192.0	203.0	220.0	-
Portland cement	176.0 168.0 175.0	214.25 218.00 206.00	238.0 203.5 239.0	215.0 220.0 219.75	261
Average	173.0	212.75	208.5	218.25	261

APPENDIX 2

Compressive strength values of 1:3 mortar cubes of supersulfated cement compositions.

Composition	Compressive strength (kg/cm^2)				
	1 week	2 weeks	3 weeks	4 weeks	12 weeks
Composition IV (85% slag, 10% plaster of Paris, 5% Portland cement)	39.0 30.0 29.0	174.0 155.0 166.5	191.0 190.0 190.5	209.0 207.5 198.5	325.0
Average	89.3	165.1	190.5	205.0	325.0
Composition V (80% slag, 15% plaster of Paris, 5% Portland cement)	102.0 100.0 98.0	237.0 200.0 -	281.5 275.0 278.5	301.0 278.0 280.0	300.0
Average	100.0	203.5	278.3	286.3	300.0

APPENDIX 3

Compressive strength values of 1:3 mortar cubes of supersulfated cement composition VI.

Composition	Compressive strength (kg/cm^2)				
	1 week	2 weeks	3 weeks	4 weeks	12 weeks
Composition VI (80% slag, 15% plaster of Paris 5% hydrated lime).	82.5 89.0 89.5	106.0 110.0 108.0	106.5 109.5 105.0	115.0 96.0 95.0	120.0
Average	87.0	108.0	107.0	102.0	120.0

APPENDIX 4

Compressive strength values of 1:3 mortars of supersulfated composition V - Bo .

Composition	Compressive strength kg/cm^2				
	1 week	2 weeks	3 weeks	4 weeks	12 weeks
Composition V - Bo	60.0	156.0	178.0	208.0	
(80% slag, 15% plaster	62.5	126.0	200.0	255.0	323.0
of Paris 5% Portland	47.75	168.0	240.0	321.0	
cement+ 0.2% borax by					
weight of cement).					
Average	56.75	150.0	220.0	289.5	323.0

APPENDIX 5

Compressive strength values of 1:3 mortars of supersulfated cement composition VII .

Composition	Compressive strength kg/cm^2				
	1 week	2 weeks	3 weeks	4 weeks	12 weeks
Composition VII	95.0	131.0	-	162.5	
(80% slag, 15% hard-	85.0	130.0	154.0	157.0	210.75
burnt gypsum,	90.0	131.5	140.0	160.5	
5% Portland cement)					
Average	90.0	131.8	147.0	160.0	210.75

APPENDIX 6

Chemical composition of Kalinga blastfurnace slag.

Oxide	wt %
SiO_2	30.2
Al_2O_3	30.0
CaO	32.0
MgO	5.6
MnO	1.8
FeO	0.9

APPENDIX 7

Compressive strength values of 1:3 mortar cubes of supersulfated cement composition V using Kalinga slag.

Composition	Compressive strength Kg/cm^2				
	1week	2weeks	3weeks	4weeks	12weeks
Composition V	38.0	84.0	150.0	160.0	-
(80% Kalinga slag,	41.5	80.0	170.0	204.0	235.0
15% plaster of Paris,	42.0	81.0	165.0	193.0	
5% Portland cement).					
Average	40.5	81.6	161.6	185.6	235.0

APPENDIX 8

Expansion/shrinkage of supersulfated concrete
 (1 part composition V cement, 4 parts fire brick grog)
 on heating/cooling.

Temperature °C (Heating)	Dilatometer reading mm.	Temperature °C (Cooling)	Dilatometer reading mm.
100	0.04	700	0.46
200	0.12	600	0.39
300	0.20	500	0.31
400	0.33	400	0.25
500	0.45	300	0.10
600	0.54	200	0.06
700	0.56	100	0.03
800	0.58		

APPENDIX 9

Tensile splitting and compressive strength values of supersulfated and alumina cement concrete pellets

Composition: 1 part cement, 4 parts fire brick grog
Water/cement ratio: 0.6

Temperature °C	Supersulfated cement concrete			Alumina cement concrete		
	Tensile splitting strength Kg/cm ²	Compressive strength Kg/cm ²	Average compressive strength Kg/cm ²	Tensile splitting strength Kg/cm ²	Compressive strength Kg/cm ²	Average compressive strength Kg/cm ²
Room temperature						
100	8.17	81.7	81.7	19.34	193.4	193.4
	5.05	50.5	55.2	18.08	180.8	
300	6.00	60.0		16.45	164.5	172.6
	2.18	21.8				
500	-	-	21.8	11.97	119.7	106.2
	1.86	18.6		9.27	92.7	
700	-	-	18.6	7.00	70.0	69.8
	1.51	15.1		6.96	69.6	
900	1.93	19.3	17.2	9.12	91.2	72.7
	2.10	21.0		5.42	54.2	
950	1.83	18.3	19.6	17.12	171.2	164.6
	12.86	128.6		15.8	158.0	
1000	9.96	99.6	114.3	-	-	-
	16.01	160.1	160.1	-	-	-

